AMERICAN
DYESTUFF REPORTER

VOLUME XXIII JUNE 4, 1934 NUMBER 12

The Importance of

Copper in Textile Technology

By ARTHUR H. PETTINGER, B.Sc., A.I.C.

COPPER exerts its effects in other spheres than textile technology: for instance, it is sometimes a contributory cause of "haze" in beer; and its presence has been detected in cancers and tumors. Such points as these are not of direct interest to textile men, but serve to illustrate how active a catalyst copper can be on occasions.

A previous article dealt with Iron from the standpoint of the point of view of textile chemistry and dyeing. It is now proposed to review the uses and peculiarities of Copper from the same angle. Like Iron, Copper is a common material for the construction of technical equipment, and on account of its low price (relatively) it is very widely used and its chemical properties are consequently of great importance. It appears, moreover, in "traces" in various materials and exerts a powerful catalytic action in chemical processes and so a study of it is both interesting and vital.

One of the uses of copper sulfate almost everyone is familiar with is that of the aftertreatment of direct cotton colors and sulfide colors. After the goods have been dyed in the ordinary way, they are rinsed and dipped in a fresh bath for half an hour at 140-175 deg. F. containing about 2 per cent of copper sulfate and 2 per cent acetic acid. This improves the fastness to light. Fast Yellow GK, Fast Red F, and Sky Blue FF types of colors are improved by coppering.

The firm of Meister Lucius and Bruning used to market a few wool colors that could be developed with copper sulfate, e.g. their Copper Red N, Copper Blue B, and Black S. These colors were dyed with the usual vitriol and Glauber's salt and developed up with 2 per cent copper sulfate. The resulting shades were cheap, very fast to light, and suitable for piece-dyeing where no great fastness to milling was required.

In the dyeing of aged aniline black, copper is used as an oxygen-carrier. The goods are padded with a mixture of aniline hydrochloride solution, an oxidizing agent such as chlorate of soda, and an oxygen carrier as, for instance, copper sulfate or sulfide, one part per ten of aniline hydrochloride. Blacks produced this way are faster and less liable to green than by the single bath process.

Sulfate of copper finds a limited field of application in the dyeing of logwood on wool. Acting alone, as a mordant, it gives greenish-blue to black shades with logwood, but it is also used in combination with bichrome and sulfuric acid as an oxygen carrier in the dyebath. Bonsor's formula for a logwood black requires the use of copper sulfate along with bichrome and sulfate of iron.

Applied to cotton, a little sulfate of copper is added to the iron mordanting bath, as it tends to prevent logwood blacks turning to a rusty appearance.

Unfortunately, the presence of copper is not always to be desired in textile operations; there are a large number of cases where it is definitely injurious, and it is proposed to deal with these briefly.

As a material for the construction of dyebaths, copper is not often used, but none the less, this metal frequently finds its way into solution from brass or similar fittings, steam pipes, washers, etc., and the effect on the resulting shade is to make it duller and even render it entirely different from what is intended. After an hour's boil, a dyebath containing the usual proportion of vitriol may take up 1 part in 200,000 of copper. Dyers of loose wool and fur often use vats made of copper, so in this case there is a correspondingly higher risk of interference. The addition of 4 ounces ammonium sulfocyanide per 100 gallons of liquor previous to dipping the goods will go a long way to prevent it, however.

Generally speaking, acid colors are very sensitive to copper, but there are exceptions, and makers of colors are always prepared to make suggestions as to the best

ones for any particular purpose. Mention may be made of four colors which are listed to be of good resistance to copper, namely, Quinoline Yellow, Chlorazol Fast Red FG, Alizarin Brilliant Green, Alizarin Sky Blue B.

Direct or substantive, cotton colors are also sensitive to the metal, but the risk of dissolving it from the dyebath fittings is not so great as dyeing is usually conducted neutral or on the alkaline side.

Grundy (1929) found that basic dyes could be successfully applied to fibers in the presence of copper, as could also most vat dyes and azoic colors. In the case of sulfide dyes, copper was unsuitable as black copper sulfide was, of course, formed.

Of general interest are the results he obtained, showing the effect of acid and alkali on copper. Boiling 0.2 per cent of vitriol caused a copper surface to lose 30 grams per square meter in 8 hours. Caustic soda solution composed of 4 parts, 66 deg. Tw. per 100 water for the same time at 80 deg. C. produced "little change".

Copper has been found to be at the bottom of a number of dyeing faults. Ravizza (1914) records the formation of brown to olive colored stains in union material prepared from cotton and shoddy. The latter material proved to have been prepared from material used for theatrical purposes and to contain copper. During carbonization, the meta particles had been dissolved and dispersed by the vitriol used. The staining was shown to be due to the combination of copper and sulfides formed in the alkaline washing of wool, and also to the formation of copper oleate when the goods were oiled with olein.

A peculiar form of discoloration of wool due to previous alkali damage has been recorded by N. D. White. Wool which has received unduly heavy scouring or alkali treatment is subject to yellow streaks when dyed in a bath containing traces of copper in solution, presumably due to the localized formation of copper sulfide. Suggestions as to prevention are to be found in the original article (Dyer. September 1933).

Copper has long been known to be injurious if present in fabrics which are bleached with peroxide and perborates. P. Heerman drew attention to the risk of tendering in this connection several years ago due to iron or copper stains on the fabric. These substances decompose peroxides with liberation of oxygen at the affected places, and the formation of oxycellulose naturally follows. His views have not passed unchallenged, however, for Brauer (1925) says that, on the contrary, bleaching with peroxides may be performed in copper vessels without damage, and asserts, also, that soap detergents containing peroxides are more efficient than ordinary soap for coffee, milk, or cocoa stains. Dalstrom also says that the presence of copper and iron salts together promotes deterioration, but that iron alone does not. In the presence of sodium soaps these metals do not exert their catalytic properties and may be bleached with safety and satisfaction. His conclusions are certainly worth serious consideration. Bleaching is usually conducted in stoneware or Monel in actual practice.

Copper is a particularly undesirable metal where rubber is concerned and fabrics which are to be proofed and treated with latex must not contain more than 0.01 per cent. In fact, so energetic is copper as an oxygen carrier in rubbered fabrics that there is a definite risk of fire, according to Fol and Visser. The rubber on cloth usually presents a large surface to the air, another contributory factor in oxidation. It is said, however, that aniline black dyed material may be safely rubbered.

To refer to milk in an article of this kind would seem a digression, but in this case it is justified by being capable of application in principle to textile wool oiling. Milk is subject to a tendency to develop a disagreeable fishy, oily taste and this has been traced to the catalytic effect of small quantities of copper as well as the action of the air. This opens up the subject of the auto-oxidation of oil sand fats, a very large subject, and metallic catalysts certainly play their part. Quinol and napthol are substances which are known to aid oils to resist oxidation and drying. Thus, to take a familiar example of a drying oil, linseed oil, a Russian chemist has recently noted that the addition of one per cent of beta-napthol restrains the oxidizing tendency, and the iodine value of viscosity remain constant for two years.

The textile application is seen in a recent patent (U. S. Patent 1791057) of A. H. Gill of Belmont, Mass., 1931. Unsaturated oils are much used for wool lubrication, e.g., olive and red oil, and in the presence of metallic catalysts there is the danger of rapid oxidation and ultimately combustion. The claimant proposes to add 1 to 2 per cent of a polyhydric phenol, such as quinol, and thereby reduce the fire risk in storing wool in the oil. Apart from the danger of fire, there is the tendency of certain oils to go thick, tacky, and smell badly, when they become extremely difficult to scour out. It seems probable that the addition of a phenolic anti-oxidant might prevent this too, enabling a much lower grade oil to be used than otherwise. Quinol is reported to have been added to almond and lard oils to prevent rancidity.

Copper salts are very toxic to micro-organisms and are to be avoided where ferments are concerned. The use of amylases in textile work for liquefying starches prior to application in sizing and finishing is already well known. Copper vessels must be avoided. This also applies to the use of ferments in de-starching rayon goods, etc. In brewing, for instance, this metal is liable to poison the yeast. It has also a marked effect on enzymes; in bottled beer it tends to disturb the equilibrium between the colloidal constituents and precipitate "haze".

This toxic property has been put to good account in the purification of water. Thus, copper sulfate is added to the contents of reservoirs to destroy odor-producing algae, and it is said to be without action on fish. Hale,

in 1930, reported the use of one pound copper sulfate per million gallons of water.

A simple method of sterilizing water for domestic use has been described by Kraemer, involving the use of a sheet of metallic copper in the tank, 3½ inches square per quart of water, 6 hours. B. Coli and B. Typhosus bacteria are said to be killed by this treatment. Kraemer's statements are not universally accepted, however, and the method is not much used, if at all.

A very little-known reaction of copper is its behavior inside a boiler. Where the water evaporated contains appreciable quantities of sodium salts, and also has dissolved in it oxygen, copper catalytically increases the rate of rusting of the boiler plates. In the absence of dissolved oxygen the corrosion caused in this manner is small and negligible. Water supplies containing such heavy metals as copper and iron also are to be used with caution.

Having now studied the unfavorable properties of copper in some detail, let us turn to the more positive side, that of its useful qualities and modes of application.

In the manufacture of cuprammonium rayon, this metal is used in large quantities. Cotton, freed from its impurities by boiling in alkali under pressure, is bleached and then, while wet, is dissolved in Schweitzer's reagent. This is obtained by the interaction of copper turnings and dilute ammonia, air being bubbled through meanwhile. This solution slowly dissolves cotton when in contact with it a few hours, and a thick blue fluid is obtained. The cellulose is regenerated by forcing the solution through fine nozzles into a coagulating agent of acid or other similar preparation. Many refinements over and above this skeleton outline are, of course, used in practice.

Cuprammonium, or Schweitzer's reagent, has other uses besides this. As a dope, it is sometimes applied to the fabric of aeroplane wings, and it is also used to aid the examination of cotton and other vegetable fibers under the microscope. The cuticle or outer coating of the cotton hair is somewhat insoluble in cuprammonium and the partly dissolved cellulose in the interior swells up. This process can be followed conveniently on a glass slide with a high-power objective.

A very important part of textile chemical analysis is the determination of the "Copper Number" of cellulose materials to find out the degree of damage which they have received in bleaching. Schwalbe's original method (1907) consists of boiling a 3 gram pattern of the material in a flask with 100 c.cm. of Fehling solutions and 200 c.cm. of water. To prevent evaporation, a reflux condenser is fitted. Boiling is continued for 15 minutes, when the mixture is filtered, the residue of cuprous oxide washed well and dissolved in nitric acid and copper determined electrolytically. The "Copper Number" is then calculated, being the weight of copper reduced by 100 parts of dry cotton. Pure bleached cotton which has not been over-bleached, gives a number of about 0.5, but if the treatment has been excessive, higher figures are obtained, up to a maximum of 15, the figure itself being, broadly, a measure of the oxycellulose which has been formed.

A great many modifications of Schwalbe's method have appeared in the literature from time to time. Knecht and Thompson (1920) dissolve the cuprous oxide in sulfuric acid and add it to a solution of ferric alum. The amount of iron thus reduced is determined by titration with standard potassium permanganate. Instead of Fehling's solution, a mixture of copper sulfate, sodium carbonate and bicarbonate has been used with success by some authorities.

Cotton which has been mercerized is more soluble in Schweitzer's reagent than normal cotton, but this fact is not of great value in doubtful cases. A new test by Birtwell, Clibbens, Geake and Ridge of the Shirley Institute enables small changes in cotton to be readily detected. It consists in determining the copper number after the pattern has undergone oxidation treatment with alkali hypobromite under certain specified conditions. Ordinary white cotton fabric gives a value of 1.5, but for cotton which has received swelling treatment such as mercerization the value is 1.6 or thereabouts. Consistent and accurate results can be obtained by this method.

Another notable advance in the chemistry of cellulosic materials is that of Clibbens and Ridge (J. Tex. Ind. 1928) who have established a dependable scientific test of latent deterioration in cotton material which has undergone oxidizing treatment. Copper number gives only an approximate idea of oxycellulose damage; the new test is a marked improvement and is of value in those cases where the damage in cotton is only made evident upon washing. Briefly, the method consists in measuring the fluidity of a 0.5 per cent solution of the pattern dissolved in cuprammonium.

Thus we have seen how important a metal is copper in a textile works laboratory, but there remains to be found a suitable name to cover all these methods of analysis with copper. What about Textile Cuprimetry?

In the sphere of dyestuff application, copper and its salts may be used as catalysts and as oxygen carriers. One recent Patent (B. P. 310,472) employs this property of assisting oxidation in the application of vat dyes. The material is treated with a mixture containing copper sulfate, tragacanth and formic acid. This is followed by the application of the ester salt of a leuco vat color. No special process of re-oxidizing the color is then needed, ordinary drying being sufficient, the copper present supplying the necessary oxygen.

A large number of patents have appeared in which the metal is made use of in dye manufacture. For instance, in the production of sulfur colors, the Atkien-Gesellschaft fur Anilin-Fabrikation find that the addition of copper to

the reaction mixture enables dyes to be obtained of clearer, brighter shades. It is found that complex salts are also efficacious, potassium cuprocyanide K_6 [Cu_2 $(CN)_2$] being specified as particularly suitable and free from the tendency to form compounds with the sulfide present in the mixture. Very vivid clear-toned dyes are said to be obtainable along these lines. (B. P. 235,556).

Quite a considerable number of patents relate to the manufacture of direct cotton colors which contain copper in the molecule and so are of great fastness to light and washing; no after-coppering being obviously necessary. For example, B. P. 245,128 of the I. G. Farbenindustrie describes the preparation of dyes which may be united with Copper and dyed direct onto cotton. B. P. 297,003 of Soc. Chem. Ind. Basle relates to the manufacture of dyes containing both copper and chromium. One example cited, dyes cotton in a neutral or alkaline bath fast reddish blue tints. A violet dye is also described.

The difficulty of getting level-dyeing shades for viscose is well known. The use of copper containing dyes for this class of work is consequently of great interest. B. P. 300,916 deals with the coupling of an O. Amino-phenol with a J. acid derivative, and B. P. 315,664, the coupling of an O. Aminocarboxylic acid with J. acid derivative, to obtain a product which may be combined with a coppering agent to form a complex metal compound which dyes viscose in even shades. B. P. 288,307 and 306,908 of the I. G. Farbenindustrie also describe the manufacture of complex copper dyestuffs.

Copper has many uses as a catalyst in organic chemical reactions. Numerous recent patents refer to the use of the metal or its salts in the intermediate manufacturing trade and a comprehensive account of this subject would fill a great many pages. It is not proposed to deal with it at such length, but to refer, briefly, to a few patents as indicating the extensive application of copper.

In the production of acetic acid from carbon monoxide several patents mention copper oxide, copper acetate amongst other catalysts for assisting the reaction, for example (B. P. 264,558 and 268,845).

According to H. Dreyfus (B. P. 345,271) a copper tube is used, filled with barium hydroxide, for the preparation of acetone from ethyl alcohol vapor.

A copper catalyst activated by alkaline oxides and/or thoria alumina, etc., is of use in the isomerization of glycols to ketones (B. P. 318,124 of the I. G. Farbenindustrie A-G.).

Zinc cyanamide containing 1 per cent of copper sulfate is proposed by the Imperial Chemical Industries as catalyst in the synthesis of hydrocyanic acid from ammonia and carbon monoxide (B. P. 305,816).

Waterproofing processes in a few instances involve the use of copper soaps, such as, for instance, sail cloth, wagon sheets, etc. The cloth is run through a bath of soap containing about 2 pounds per 10 gallons, the temperature being 100 deg. F. It is then squeezed between rollers and direct into a cold solution of copper sulfate made up on 3½ pounds per 10 gallons. A small admixture of a green basic dye is occasionally made.

Copper soaps and allied compounds are often prepared with a view to their use in preventing mould and bacterial deterioration, apart from the proofing qualities. Fishing nets may be impregnated with copper oleate dissolved in a solvent to prevent the decay of the fiber as a result of sun, rain, sea water, marine organisms, but this preservative action is not permanent; unsaturated oils from fish exert a certain solubilizing action on the copper soap. However, there is still some doubt whether copper treated fabrics, for roofing, for example, last any longer than other kinds not so treated. Whatever we may think regarding the value of copper in preserving against the effects of sunlight, air, etc., there are still ample grounds for believing that it prevents bacterial attack in cellulose goods. A recent patent (B. P. 341,092), employs a mixture of the fluoride and sulfate of copper with a phenol or napthol for impregnating and preserving cellulose materials. In another, F. H. Cotton and Wakeley Bros. (B. P. 345,468) treat sacking with copper sulfate tinted with Brilliant Green Crystals, followed by a mixture of silicate and soap. This is claimed to prevent rotting.

Hair dyeing is a subject which is hardly within the legitimate scope of a textile dyer, but, here again, copper may be used. Copper chloride 1 part, pyrogallol 1 part, dissolved in water 100 parts, is applied. The shade effected is brown and the dye is claimed to be odorless.

A rather curious application of copper is as a tonic medicine when taken in conjunction with iron. Thus in the treatment of anaemia, pure iron is ineffective, but with the addition of small amounts of copper it becomes effective. Based on this principle, the infant food "Virol" contains copper.

It is well known that small traces of certain metals exert a profound effect in animal and plant cell processes, but one would not otherwise associate cancer with copper. Cancer cells are known to grow and multiply independently of their victim and at a comparatively rapid rate. An article appeared in the "Lancet" some years ago, when the high proportion of the metal in tumors and growths was noted. As much as 500 mgm. of copper per kilo. of tissue was found in one instance, and the author asked, quite naturally, if it is not possible that the catalytic action of copper was playing some part in the cell degeneration. Whether the copper is the cause or merely the effect of the cancer one would not like to say. A certain amount is found everywhere however; in the human body and for instance, in meat, egg yolk, etc. We may yet learn something new about the chemistry of copper from our pathologists!

One important means in which copper is used is in Monel metal which contains about 29 per cent of copper

(Continued on page 332)

PROCEEDINGS OF THE
American Association of Textile Chemists and Colorists

JUNE 4, 1934

Officers of National Association

ROBERT E. ROSE, *President*
E. I. Du Pont de Nemours & Co., Wilmington, Del.

A. R. THOMPSON, Jr.—ALEX MORRISON, *Vice-Presidents*

WILLIAM R. MOORHOUSE, *Treasurer*
National Aniline & Chemical Co., Boston, Mass.

HAROLD C. CHAPIN, *Secretary*
Lowell Textile Institute, Lowell, Mass.

Councillors

JOSEPH F. X. HAROLD — **WILLIAM D. APPEL**
DONALD H. POWERS — **HUGH CHRISTISON**
CARL Z. DRAVES — **WALTER M. SCOTT**

President Emeritus and Chairman of the Research Committee

LOUIS A. OLNEY
Lowell Textile Institute, Lowell, Mass.

Council Representatives: Northern New England—Roland E. Derby, New York—Hans Meyer, Philadelphia—Harold B. Dohner, Midwest—Carl E. Bick, South Central—G. H. Dubois.

Local Sections and Their Officers

Northern New England Section
Leverett N. Putnam, Chairman, Worsted Division, Pacific Mills, Lawrence, Mass.
Clarence L. Nutting, Secretary, Arlington Mills, Lawrence, Mass.

Rhode Island Section
Heyward F. Lawton, Chairman, Borden & Remington Co., Providence, R. I.
C. Brian Wainwright, Secretary, Apponaug Co., Apponaug, R. I.

New York Section
Henry F. Herrmann, Chairman, General Dyestuff Corp., 230 Fifth Ave., New York City.
Thomas R. Harris, Secretary, Herrick & Voigt, 21 West St., New York City.

Philadelphia Section
William A. Stringfellow, Chairman, Ankokas Mills, Mount Holly, N. J.
Charles A. Seibert, Secretary, 39 Chestnut St., Salem, N. J.

Piedmont Section
George P. Feindel, Union Bleachery, Greenville, S. C.
John C. Robertson, E. I. du Pont de Nemours & Co., 5 Pettigru St., Greenville, S. C.

South Central Section
Harold Schroeder, Chairman, Dixie Mercerizing Co., Chattanooga, Tenn.
Harvie Bruce Kimbell, Secretary, Dixie Mercerizing Co., Chattanooga, Tenn.

Midwest Section
Eric F. Hempel, Chairman, National Knitting Co., 2165 South First Street, Milwaukee, Wis.
Elmer F. Smith, Secretary, American Aniline Products, Inc., 820 S. Clinton St., Chicago, Ill.

South-Eastern Section
Charles B. Ordway, Chairman, Alabama Polytechnic Institute, Auburn, Ala.
C. A. Jones, Secretary, Georgia School of Technology, Atlanta, Ga.

Lowell Textile Institute Student Section
Raymond L. Matthews, Chairman; Charles L. Daley, Secretary.

North Carolina State College Student Section
H. S. Blinens, Chairman; D. B. Hardin, Secretary.

Members should notify the **Secretary** immediately of all address changes

A New Product

Soft Hard Water*

By **G. W. SMITH**[1]

RALPH E. HALL, to whom are due the recent advances in chemistry of the metaphosphates to be outlined tonight, has pointed out that the impurities in water did not become the object of systematic study until growing industry met the handicaps of impure water. In earlier days, beneficiation of water may have been practiced, but with inspired empiricism at best; records are few, and one of the earliest is Exodus XV, 23-25, to which Rideal has drawn attention. Watt's invention of the engine with its boiler was predestined to lead to scientific and engineering investigation of the origin of the calcareous deposits left behind in the boiler by the effluent steam. Boiler scale has ever since assumed a large and increasing importance in industrial development. Bigger boilers, higher steam pressure, more intensive working of heating surfaces and more rigid specifications for steam quality have made imperative today's high standard of boiler water conditioning.

Surely of no less importance in focusing intelligent attention on quality of water was the industrial revolution in England, inaugurated by Arkwright's invention and the mechanization of the loom, sometimes aided by Watt's engine, whereby textile operations were centralized and, perhaps unfortunately, water troubles as well. Here also the lime and magnesia content of natural waters has been irksome at best, and at worst impossible of tolerance. During the first part of the nineteenth century progress began in the direction of water-softening whereby the bulk of the calcium and magnesium could be removed, which, continued to the present day, has given us artificially soft waters containing a grain or less of hardness per U. S. gallon. Softened water has been almost the

* Presented at March 2nd Meeting, N. N. E. Section.
[1] General Manager, The Buromin Company, Pittsburgh, Penna.

salvation of certain types of textile processing, but softening alone and as practiced today is not a complete or final solution to the requirements of all.

Passing by for the moment the "residual hardness" in softened waters let us note certain of the other impurities of importance. These are a diverse group. Iron, both ferrous and ferric, and occasionally manganese, present to the extent of a part per million or so are of little moment in boiler water conditioning, but have serious consequences in textile operations. Bicarbonate content of raw and zeolite-softened water, and hydroxide and carbonate content of lime-soda softened waters, affect the use of the water for scouring, laundering, and rinsing. Dissolved gases, particularly oxygen, affect indirectly and through corrosion of piping, the quality of water delivered to the point of use. Organic material, often oxygen-consuming and thereby subject to chemical change in dyeing operations, is occasionally present and its significance may not even yet be fully recognized.

The presence of small proportions of heavy metals has been thought to lead to corrosion of aluminum; spectroscopic determination may be employed to show the presence or absence of these elements.[2] The Treasury Department Standards for Drinking Waters recognize and forbid the presence in natural waters supplied by common carriers for drinking purposes of lead in excess of 0.1 ppm., of copper in excess of 0.2 ppm., and of zinc in excess of 5.0 ppm.[3] Those of my audience are more familiar with the injurious effect of these metals in textile operations than am I, and the possibility of their presence in water supplies for these uses deserves attention. Fluorine, long neglected as a possible constituent of drinking water has been found in the (to the water chemist) relatively large concentration of several parts per million.[4] It is responsible for grave flaws in dentition of children, and its presence, physiological properties, and removal, have been the subject of several journal articles. As an extreme instance of minute but significant impurity one can cite the recommended maximum concentrations in potable water of some types of organized protoplasm. It is desired that not more than an average of one *B. coli* be present in each 100 ml. of drinking water. On a weight basis, this is roughly one part per 17 million billions, or one pound of this impurity in 2,000 cubic miles of water. The bacteriologists are to be complimented on the sensitivity of their analytical methods.

Heavy metals, lead, copper, zinc, fluorine and B. coli may be of debatable importance to the textile chemist on account of their infrequent occurrence, but calcium and magnesium are not, even in so-called "soft" waters. A convenient unit for computation is a million gallons. Let us visualize a million gallons of water as filling a cubical tank about 52 feet on an edge. If we assume that it is relatively soft and contains 7 ppm. Ca,[5] we may compute the amount of calcium present in our unit quantity of water. If isolated in metallic form we could have a cube of calcium approximately 10″ x 10″ x 10″. This may not seem a large quantity, but if instead of isolating metallic calcium, we were to precipitate the calcium by soap, we would have over 850 pounds of anhydrous lime soap, enough to fill a bath tub, or enough if it could be properly applied, to provide a water-repellent mono-molecular coating over an area about three times as large as Manhattan Island.[6]

Difficulties with lime soap were common before the concept of mono-molecular films was invented, and are no less real today. The adverse effect of insoluble soaps and calcium and magnesium precipitates on textiles has made desirable the use of soft water, and the gross waste of soap when it is used in hard water has provided the economic compulsion for the installation of softeners. Improvement in product and economy in process has ensued.

It is only in certain sections that waters are naturally as soft as that taken above for an example. A hardness of one grain per gallon is the limit of effectiveness of the best lime-soda softener. A zeolite softener, properly operated, will do somewhat better. In neither case is the water so free of hardness that the precipitation of metallic soaps will not occur. That this is so is due to the great insolubility of lime and magnesium soaps when expressed in terms of equivalents, and can be verified by reference to Seidell or by simple experiment. If one takes hard water, adds thereto slightly more than the quantity of soda ash or tri-sodium phosphate requisite for softening, and allows time for precipitation and settling, the softening is presumably completed. If a portion of the clear softened water be decanted into a bottle and a soap test made, the hardness will be found much reduced with but a grain or so residual hardness remaining. If the portion taken for test contains its proportionate share of sludge, a different effect is observed. Only a transient softness obtains; the lather disappears, rapidly when tri-sodium has been used, more slowly with the crystalline calcium carbonate precipitate, and more and more soap solution must be added. If sufficient time be given, almost as much soap solution will be used as was required by the untreated hard water. The explanation is, of course, simple. Calcium soap is less soluble than calcium phosphate or carbonate in equivalents per liter, and in the

[2] Private communication from Mr. H. V. Churchill.

[3] Standard Methods for the Examination of Water and Sewage, A.P.H.A. Seventh Edition, 150 (1933).

[4] Churchill, H. V., Occurrence of Fluorides in Some Waters of the U. S. Ind. Eng. Chem. *23*, 996 (1931).

[5] Approximately one grain per U. S. gallon of calcium hardness (as $CaCO_3$).

[6] The Borough of Manhattan has an area of 14,209 acres.

presence of sodium soap, these precipitated calcium salts redissolve and calcium soap precipitates.

Suppose one were to treat hard water with a granular zeolite. If the treated water be removed from the zeolite, and tested for hardness, it will be found soft to within the limit of accuracy of the soap test as usually conducted —about ½ grain per gallon. If on the other hand the zeolite remain in contact with the water while the soap is added, much more soap solution is required. The soap removes the hardness from the water more effectively than the zeolite, and the latter gives up its calcium and magnesium in the presence of soap. Water which has been treated with lime and soda, with phosphate, or with zeolite, and from which the calcium and magnesium have been removed, while termed "softened" water, is not soft in contact with precipitated sludge or un-revivified zeolite. The calcium is available in the water, although originating from a separate phase, and the soap seeks for it and finds it. Only two other varieties of softened water have been commercially available until recently—distilled water and its less consequential relative, frozen water. In these, by change of state of the water itself, hardness is left behind and soft water is obtained.

All these softening processes have one characteristic in common; they involve two or more phases. Either the hardness is removed from the water through the appearance of a second phase, or through base-exchange on a second phase, or the water is removed from the hardness by change of state. I wish now to draw your attention to a second type of water softening, unique in that the calcium and magnesium are not precipitated or removed from the water. No second phase is involved. A single reagent added to the water softens it completely without change in clarity of color. If to a hard water we add a sufficient quantity of this reagent and then subject the water to soap test, we find it soft. Not only is it soft; calcium chloride may be added to it and still it remains soft. We have veritably a new product, soft hard water. Hard water thus treated not only fails to precipitate lime soap; it will actually dissolve lime soap. Water containing an appropriate excess of reagent may be spoken of as having a hardness of "minus ten grains", or some other figure, because a definite amount of calcium calculated as calcium carbonate may be added to a gallon of the water before it becomes hard. The reagent is sodium hexametaphosphate, a polymer of $NaPO_3$. The discovery of its utility was made by Dr. Hall, whose publications on the subject will shortly appear, and whose work on water conditioning has recently been honored by the Pittsburgh Section of the American Chemical Society.

There are over a score of recognized sodium phosphates. The three ortho - phosphates, mono- (NaH_2PO_4), di- (Na_2HPO_4), and tri-sodium (Na_3PO_4), all salts of trivalent ortho-phosphoric acid, have been used in industry for years; the mono-sodium salt to only a limited extent. Tri-sodium phosphate has been used as a boiler-treating chemical, as a soap builder and scouring supply, and as alkaline detergent and domestic "water-softener". Di-sodium phosphate is likewise used in boiler treatment, and has large application in silk dyeing. Mono-sodium phosphate is used for boiler water treatment. The orthophosphates are the most suitable reagents available for precipitating calcium and magnesium as non-adherent sludge in boilers at moderate and high steam pressures, and hence for the prevention of adherent scale, but the insolubility of calcium phosphate which adapts them for this purpose leads to deposits in feed lines. It was this effect which led Hall and Jackson[7] to propose the use of meta- and pyrophosphates for boiler water conditioning, and to make of sodium metaphosphate an industrial chemical, commercially available. Non-conducive to deposits in feed lines and non-acid, the meta-phosphates hydrate in the boiler to form mono-sodium orthophosphate, thus providing orthophosphate radical for scale prevention and hydrogen-ion for neutralization of caustic alkalinity. The hydration reactions are the reverse to those reactions by which the metaphosphates are manufactured, which reactions we have termed "molecular dehydration" to distinguish from the removal merely of the water of crystallization.

If di-sodium phosphate be heated, water of solution or crystallization is first driven off. Anhydrous di-sodium phosphate can then lose more water to form tetra sodium pyrophosphate:

$$2Na_2HPO_4 \xrightarrow{\Delta} Na_4P_2O_7 \uparrow H_2O$$

Tetra sodium pyrophosphate is a relatively stable salt, may be crystallized from aqueous solution (in which it has a pH value slightly in excess of 9.5) and is used in the textile industry as a stabilizing agent for peroxide and, I am told, as a levelling agent in the dyeing of cellulose nitrate rayon. Further heating is without effect on anhydrous tetra-sodium pyrophosphate.

If one heats the mono-sodium salt of ortho-phosphoric acid, acid sodium pyrophosphate is first obtained:

$$2NaH_2PO_4 \xrightarrow{\Delta} Na_2H_2P_2O_7 \uparrow + H_2O$$

Sodium acid pyrophosphate is likewise stable and crystallizable, and has in aqueous solution a pH value of about 4.5. It is used chiefly as the acidic constituent of baking powder. On further heating at low temperatures) it forms sodium metaphosphate:

$$\frac{n}{2}Na_2H_2P_2O_7 \xrightarrow{\Delta} (NaPO_3)_n + \frac{n}{2} \uparrow H_2O$$

The sodium metaphosphate thus formed is but poorly soluble and is variously supposed to be either monometaphosphate or a polymer in which n has a very high

[7] U. S. Patent No. 1,903,041.

value. The latter hypothesis seems more reasonable; the evolution of water at low temperature from crystalline acid pyrophosphate would be quite likely to leave a multimolecular aggregate as a skeleton of the original crystal. X-ray analysis would put it to the test.

If the insoluble metaphosphate be brought to red heat, it melts. After chilling the molten mass a highly soluble glass-like product results. It is believed that this is sodium hexametaphosphate, $(NaPO_3)_6$. This is the soluble metaphosphate first used by us for boiler water conditioning and now in more highly purified form sold to laundries and textile plants as "Calgon".

There are a large number of sodium metaphosphates reported in the literature and there are grounds for believing that the reported existence of many of them is the result of distinction without differentiation. The so-called hexametaphosphate is the most easily prepared at present, and has proven to be highly convenient in use.

Those auxiliary properties of sodium hexametaphosphate of greatest interest in textile operations will now be briefly described. Its solubility is not definitely known. As super-cooled liquid, it presents several possibilities. It may have a definite solubility in water and in addition water may have a definite solubility in the hexametaphosphate. In this case we would have a two-phase liquid system, perhaps resembling phenol and water. This point has not been definitely established, although solutions of sodium hexametaphosphate have been made containing 70% by weight of solute.

In aqueous solution sodium metaphosphate rehydrates to form sodium orthophosphate. This reaction is accelerated by increase or decrease of pH value above or below neutrality. As it is used more frequently in alkaline solution, the reversion at high pH values is of greater industrial importance than that at low pH. Nitric and hydrochloric acids are used in analytical procedures for causing reversion of meta and pyro-phosphate to ortho-phosphate. In alkaline solution high temperatures, high concentrations, high pH values, and the presence of calcium and magnesium all increase the reversion rate. A concentrated (25%) solution at normal room temperatures and at its characteristic pH value reverts about 10 per cent per month, an unimportant amount. A 2% solution at boiling temperatures, at a maintained pH value of 9.6, and in the presence of calcium reverts to the extent of 33% in 5 hours.

The pH value of pure sodium hexametaphosphate in dilute solution (¼% to 1%) is in the neighborhood of 5.5. The commercial product in so-called "unadjusted" form and in solutions of similar concentration has a pH value of 6.8 to 7.0. The higher pH value is due to the presence of a small quality, about 10%, of sodium pyrophosphate designedly introduced. When adjusted by the addition of 4% soda ash and 2% sodium bicarbonate in briquette form to the dry metaphosphate, the pH value of ¼% solutions in waters of moderate hardness and bicarbonate content becomes 8.0 to 8.5. High hardness, and to a lesser extent, high bicarbonate content of the water will diminish the pH value of the "Calgonized" water by a few tenths of a unit. The effect of the adjustment is to make dilute solutions somewhat less alkaline than soap, but when properly adjusted a concentrated solution is almost exactly neutral. No effort should be made to raise a concentrated solution above pH>7.2, or when diluted it will be unnecessarily alkaline.

Calgon dissolves satisfactorily and speedily by circulatory dissolution, and, in the glass form, it does so by no other method. Especially processed for removal of iron and alumina, the percentage of impurities is small for a commercial chemical. SiO_2 is present to the extent of 0.10% or less and is sometimes observed in the dissolving crock, where due to the abnormally high concentration of the solution and the bulkiness of the precipitate, it may give an erroneous impression which its harmlessness and insignificance belies. CaO and MgO may be present in amounts up to 0.2%. Fe is approximately 0.01% and Al 0.04%. These may be precipitated as hydrated oxides in concentrated solution at pH 8.0, but in dilute solution are unprecipitated at greater alkalinities. Of course, such amounts are negligible, but metaphosphate not treated for removal of iron and alumina contains much larger quantities of these impurities and has been known to lead to yellowing of textiles processed a number of times with the unrefined material.[8]

If we write the formula of sodium hexametaphosphate as $Na_2(Na_4P_6O_{18})$, a rational explanation of its unique effect can be had. In solution this large molecule can ionize to yield two sodium ions and the complex anion, $Na_4P_6O_{18}$—. The secondary ionization is very small, but nevertheless is sufficient to permit substitution of two or four of the remaining sodiums by calcium to yield $Na_2Ca\ P_6O_{18}$— or $Ca_2P_6O_{18}$—. This complex ion has indeed a very low order of ionization, so low in fact that in the presence of sufficient metaphosphate, the calcium-ion concentration is less than that in equilibrium with a saturated lime soap solution. The mechanism of "single-phase softening" will now be clear. The inner sodium of the metaphosphate is exchanged for calcium, the latter being, so to speak, sequestered in a soluble complex double salt, $Na_2Ca_2P_6O_{18}$. The very low concentration of calcium-ion in equilibrium with an excess of metaphosphate is less than that in equilibrium with saturated lime soap and much less than that in equilibrium with saturated calcium phosphate or calcium carbonate solutions. Even ammonium oxalate fails to find enough calcium-ion to produce a precipitate; so far as ordinary analytical pro-

[8] Dr. B. H. Gilmore, "The Application of 'Calgon' in Laundering." "The Starchroom Laundry Journal," October, 1933.

cedures are concerned there is no calcium (or magnesium) present and no calcium oxalate is produced. Furthermore, these insoluble materials, if present in the metaphosphate solution, dissolve in an effort to establish saturation equilibrium, and will continue to dissolve until they disappear, or until the metaphosphate is substantially saturated with calcium. A true solution is formed.

We know of no other reagent which holds calcium in so tight a complex. Calcium soap is so insoluble that it will precipitate in the presence of other salts which are known or believed to form calcium complexes. As we have seen, it will precipitate at the expense of previously formed calcium phosphate. We have in soluble metaphosphate a solvent for calcium precipitates in alkaline solution, and we have therefore a new tool for the processing of water and the improvement of textiles. Practical application of this new tool has been made quite generally under the supervision of Mr. E. B. Bell of your Association, and it is to Mr. Bell that I shall look for such details of its use in practice as you may care to request in discussion. Fundamental investigation of the effect of metaphosphate on commercial fibers with especial reference to the development of analytical methods is being carried on by the Calgonizing Fellowship at Mellon Institute of Industrial Research which is held by Dr. B. H. Gilmore. We feel that Dr. Gilmore's work will be of much interest to textile chemists when published and it is to him that I am indebted for certain of the data on which the following statements are based.

I wish now in a qualitative way to apply to the rinsing of wool a few of the principles we have used in analysis of other problems of water conditioning. I choose this process as an illustration, first, because of its apparent simplicity, secondly, because of its wide-spread application, and lastly, because it depicts the role played by metaphosphate in many operations of laundering and scouring.

At the conclusion of a soap and soda scouring operation one has a mass of wool containing large quantities of adsorbed, and perhaps chemically combined, alkali and sodium soap. Calcium in whatever form it may have been present in the unwashed wool has been removed at least in part, and is held by the water as precipitated calcium carbonate and calcium soap in deflocculated form. The final product desired is in most cases a wool free of lime and magnesium soaps, and of other insoluble lime and magnesium precipitates, and as free as possible of sodium soap and alkali. It would seem a simple matter to rinse out the deflocculated precipitates, the soap and the alkali, but during this seemingly simple procedure, a number of unexpected and hidden events may take place.

If the soap-laden stock could be immersed in a large quantity of distilled water, the deflocculated dirt and calcium and magnesium precipitates would be satisfactorily rinsed away, while soap and alkali would be desorbed. Eventually the stock would be acid to phenolphthalein, and clean. Suppose, however, it were treated with a large quantity of 10% $CaCl_2$ solution. The sodium soap which stabilizes the suspension of dirt and insoluble lime salts and soaps would be immediately precipitated, the "dirt load" would flocculate and quantities be entrapped by the work. Sodium soap and sodium carbonate sorbed by the stock would precipitate *in situ* as the corresponding calcium salts. In this case the stock would also be acid to phenolphthalein, but its inferior and unsatisfactory condition could not be denied.

Between these two extremes lies every commercial rinsing process, and in our opinion, often more closely to the undesirable extreme than is generally realized. The effect of zeolite-softened water often used by laundries, and the harder waters used in wool scouring, differs but in degree from that of a calcium chloride solution. The tenacity with which alkalies are held by textile fibers is so generally known that no citation is necessary; the fact that in practice it is sometimes necessary to rinse wool after the rinse water is neutral before the stock has reached this condition is good evidence. As natural water is brought up to the wool, the hardness is precipitated on and in the goods, and only after this has occurred, will such water serve to rinse slowly away the unprecipitated and tenaciously adsorbed alkali.

As an illustration of this:

A sample of wool after soaping, and with all excess water and soap squeezed out, contained 12 milligrams of calcium per 100 gms. of sample (by ashing). After scouring for 15 minutes with soap and soda, the calcium content had dropped to 30 milligrams. A metaphosphate solution was capable of decreasing the calcium content still further, to 22 milligrams, no doubt by effective removal of lime soap and lime precipitates, but no metaphosphate was used during the rinsing, the results of which are to be given. When the wool with its 30 milligram calcium content was rinsed for 22 minutes with water containing 6 ppm. Ca, calcium deposited to such an extent that 139 milligrams were found. After a total rinsing time of 45 minutes, the content of calcium was 151 milligrams. While it is true that the wool was then free of carbonate alkalinity, it is obvious that the carbonate was removed not alone by rinsing, but largely by precipitating it on the goods as calcium carbonate. A moderately soft water has here resulted in a decided "hardening" of the goods. One questions whether this represents the type of rinsing most desirable, and whether, following a suggestion of Dr. Gilmore, it would not be wise to copy the practice of the laundry, cut short the rinsing time and destroy the remaining alkali by acid neutralization, making sure only that soap is removed as completely as possible before the souring operation. If not removed, it will be decomposed by the acid with consequent precipitation of dirt and fatty

acid. This is practicable but must be done properly, due to the possible precipitation of lime soap during the early rinsing, either from soap adsorbed on the goods, or worse, by soap in contact with the goods and carrying dirt in suspension. The effective procedure would seem to be the use of absolutely soft water at this stage until soap and soil has been adequately removed, followed by the souring operation.[9]

Neglecting for the moment the soap which may be present, it is interesting to compute, on the basis of broad assumptions, the probable extent of calcium deposition in an alkaline fabric during a continuous hard-water rinse. The assumptions we will make are that one chemical equivalent of Na_2CO_3 is present on a certain quantity of wool, that in either distilled water or water containing small amounts of salts other than those of calcium and magnesium, the carbonate instantly partitions itself between wool and water according to the Freundlich adsorption isotherm, and that in two hours of continuous rinsing with distilled water, the adsorbed Na_2CO_3 is reduced to .05 equivalent which will represent saitsfactory rinsing. The further assumption is made that CO_3 on the wool is precipitated by calcium *in situ*.

The progress of the distilled water rinse will be represented by some such curve as is shown in Figure I.

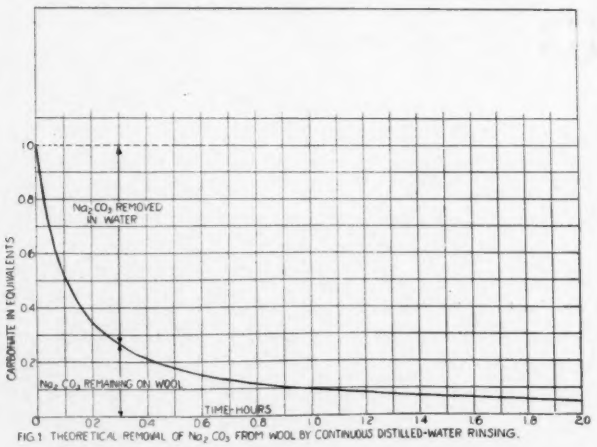

FIG. 1 THEORETICAL REMOVAL OF Na_2CO_3 FROM WOOL BY CONTINUOUS DISTILLED-WATER RINSING.

If a slightly hard water be used for rinsing, the progress of events will be as shown on Figure 2. A water has been chosen of such hardness that the calcium content in two hours' flow would just precipitate all of the Na_2CO_3 on the wool if none were removed by rinsing. This is a water of only slight hardness.

Note that the presence of calcium has permitted complete removal of the carbonate alkalinity (down to the alkalinity of $CaCO_3$) in .615 hour, whereas with distilled water under similar conditions, two hours were required

[9] The use of alkalies such as sodium hydroxide, ammonia and the like as soap builders may suggest itself for the avoidance of precipitation of insoluble inorganic calcium deposits. This will not work, however, as such alkalies precipitate calcium carbonate from a water containing bi-carbonate hardness.

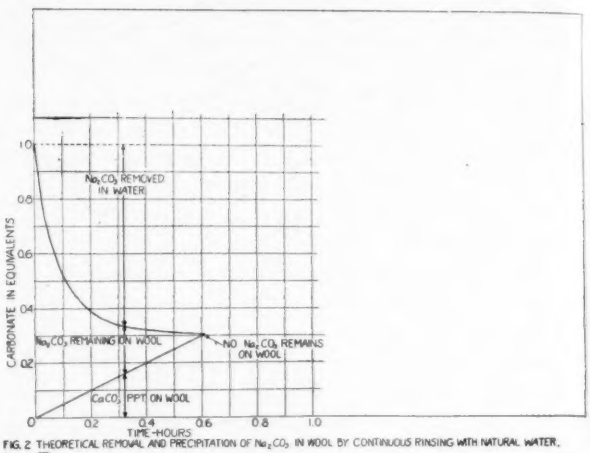

FIG. 2 THEORETICAL REMOVAL AND PRECIPITATION OF Na_2CO_3 IN WOOL BY CONTINUOUS RINSING WITH NATURAL WATER.

to reduce the sodium carbonate to 5% of its original value. This has been accomplished, however, by precipitating 30.7% of the carbonate on the fiber as calcium carbonate. If distilled water has been used, there would be left on the goods at the end of .615 hours only 14.6% of the original alkali, all as sodium carbonate.

The efficacy of slightly hard water in reducing alkalinity, as well as its allied tendency to deposit insoluble calcium salts on the goods are both evidenced by these figures. With hard water, only 69.3% of the sodium carbonate has been taken away with the rinse water; with dead soft water, 85.4% in the same time.

If a water four times as hard be used for rinsing, Figure 3 is illustrative.

In 15¾ minutes all the alkalinity is gone. 52.2% has precipitated at the goods, and 47.8% has been rinsed away. In the same length of time, with dead-soft water, 71.3% would have rinsed out.

The equations on which these curves are based are derived as follows: Sodium carbonate has been used only as an example; sodium soap could have been used just as well.

The isotherm is: $\frac{x}{m} = kc^{1/n}$,

where x is the amount adsorbed; m, the amount of adsorbent; c, the concentration in solution; and k and n are constants, $\frac{1}{n}$ often lies between 0.3 and 0.7, and for qualitative results, we assume herein that $\frac{1}{n} = 0.5$. Let $m = 1$ (unit mass of wool) and $x_0 = 1$ (unit mass of Na_2CO_3). Constant k will take care of any difference in magnitude of units. Further suppose that x_0 has been adsorbed from a solution N/10 with respect to Na_2CO_3. We then have $x = kc^{0.5}$ and $x_0 = 1 = k(0.1)^{0.5}$. From these $x = (10C)^{1/2}$.

Let distilled water be forced through the wool so that it reaches equilibrium during its passage therethrough. After the amount of Na_2CO_3 on the wool has been reduced to some value x, consider the effect of the increment of water $\triangle w = K\triangle t$ (t being time) whereby a quantity of Na_2CO_3, $-\triangle x$, will be removed. The concentration in the solution will be $-\frac{\triangle x}{\triangle w}$, and $x = (-10\frac{\triangle x}{K\triangle t})^{\frac{1}{2}}$.

Passing to the limit, and integrating:

$$\frac{Kt}{10} = \frac{1}{x} + C.$$

When $t = 0$, $x_0 = 1$; Hence $C = -1$ and $x = \frac{10}{Kt + 10}$.

To evaluate K, let $t = 2$ hours, when $x = .05$; then

$$K = 95 \text{ and } x = \frac{10}{95t + 10}$$

Figure 1 is the graph of this function.

Consider rinsing with a water of such hardness that in two hours flow, sufficient calcium would be present to precipitate all of the Na_2CO_3 which was present on the goods before rinsing.

At time t, and with the amount x of Na_2CO_3 remaining on the goods, the increment of water $K\triangle t$ will remove by rinsing the quantity $-\triangle x = \frac{Kx^2\triangle t}{10}$, and by precipitation the quantity $-\triangle x = K'K\triangle t$. K'K has the value ½, because two hours precipitation without rinsing would precipitate the amount $x_0 = 1$ of sodium carbonate. $K = 95$ (*v. supra*).

The total quantity, $-\triangle x$, of Na_2CO_3 removed from or precipitated on the wool by the water, $\triangle w$, will be $(9.5x^2 + \frac{1}{2})\triangle t$. In the limit

$$\frac{-dx}{9.5x^2 + 0.5} = dt$$

Integrating, $-\frac{1}{\sqrt{4.75}}\tan^{-1}\left(\frac{\sqrt{4.75}\ x}{0.5}\right) = t + C$

From the relation, $x = 1$ when $t = 0$, $C = -.615$.

Then, $x = \frac{1}{4.36}\tan(1.34 - 2.18t)$.

When $x = 0$, $1.34 - 2.18t = 0$, or $t = .615$ hr.

The lower curve of Figure 2 is plotted from the expression for Na_2CO_3 precipitated, $x = \frac{1}{2}t$. The upper curve is $x = \frac{1}{4.36}\tan(1.34 - 2.18t) + \frac{1}{2}t$, or the sum of the carbonate precipitated and that remaining on the goods.

Figure 3 represents the same type of curve as Figure 2, but for a water four times as hard. For this, the similarly derived equation of removal is $x' = \frac{1}{2.18}\tan(1.14 - 4.36t)$.

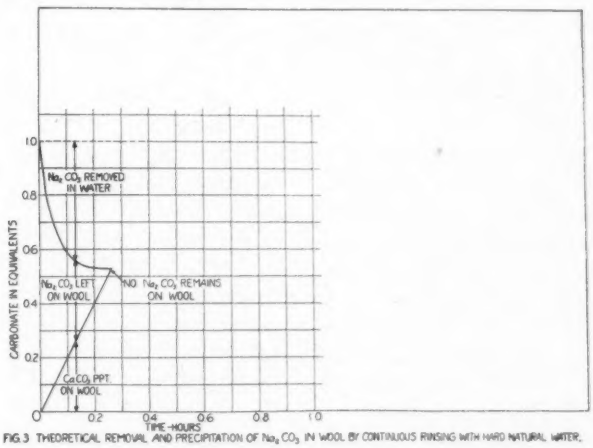

FIG. 3 THEORETICAL REMOVAL AND PRECIPITATION OF Na_2CO_3 IN WOOL BY CONTINUOUS RINSING WITH HARD NATURAL WATER.

We have only begun to consider the possible reactions at the surface of the wool fiber. There are both soap and alkali on wool at the start of a rinse, and it cannot be said definitely whether the first calcium brought in contact with the goods will precipitate soap or alkali. If the effective "concentrations" of these were known their relative solubilities could be computed using solubility product. With adequate methods, the distribution of the calcium could be determined by analysis. The more highly built is the soap, the less the amount of lime soap which will precipitate, and the greater the quantity of calcium carbonate. In view of the great insolubility of lime soap, it is doubtful whether its precipitation can be entirely avoided with natural water, either at the start of the rinse when the sodium soap concentration is high, or alternatively, later in the process when the amount of sodium carbonate has been reduced by preferential precipitation. Acid soap formation during rinsing with a bicarbonate water is a possible factor in unsatisfactory scouring, but scarcely so if the soap is properly built. These questions await the answer of appropriate analytical technic, which it is believed will be available in the near future.

Discussion

Mr. Nutting: Mr. Chairman, I'd like to ask Mr. Smith if the stability of the metaphosphate is any greater under the condition of the dye bath than it is in the soap bath at a boiling temperature, that is, in a dye bath with a pH

of 6½, is the metaphosphate stable any longer at the boiling temperature?

Mr. Smith: Sodium metaphosphate would be more stable in a dye bath at a pH of 6½ than it would be in a soap bath. The stability should be 3 or 4 times as great. The figure in the paper for reversion at pH 9.6 would be typical of the rate of reversion to be expected in the soap bath. At a pH of 6½ the dye bath would be practically neutral, which is the most favorable condition for the maintenance of calcium-repressing power of Calgon.

Mr. Dalton: I'd like to ask the effect of Calgon on the trivalent soaps, aluminum, iron and chromium.

Mr. Smith: In strong solution Calgon raises the pH value at which aluminum and iron precipitate, but not to the extent necessary to make it as important a reagent for the repression of iron and aluminum as it is for the repression of calcium and magnesium. Thus, in the absence of Calgon, iron and aluminum hydroxides begin to precipitate in the neighborhood of pH values of 3, the iron beginning to precipitate somewhat before the aluminum. In strong Calgon solutions iron and aluminum do not begin to precipitate until a pH value of approximately 8 is obtained, at which point aluminum hydroxide begins to precipitate followed at slightly higher pH values by ferric hydroxide. In dilute Calgon solutions, such as are used in textile operations, the iron does not precipitate unless perhaps in colloidal form until a pH value of approximately 10 is attained.

The effect of metaphosphate solutions on iron, aluminum and chromium salts is under investigation in several fields, but we are not yet ready to publish any of our data.

The original Calgon contained some iron and alumina, and slight yellowing was observed in textiles repeatedly washed with this material. When the content of iron and alumina was reduced to the present low value, the yellowing no longer occurred.

Question: Is Calgon of any value in kier boiling cotton when you are working with a rather high alkalinity and pressure?

Mr. Smith: At kier pressures of 30 pounds per square inch or above reversion of metaphosphate becomes a factor to be considered. Such pressures correspond to a temperature of 275° F. or above, and in the presence of the characteristically high alkalinities, the reversion rate would be materially greater than at 212° F., and at a pH value of 10. I would expect under these extreme conditions of pressure and temperature to attain a maximum reversion rate of 50% in about one and a half hours. This, of course, does not mean that the remaining 50% would revert in the next hour and a half.

If the effect of reversion were notable, Calgon could be added towards the end of the operation although it would appear from practical results that the Calgon exercises its calcium repressing and soap-dissolving properties before reversion sets in, or that the rate of reversion is less than that which would be expected.

Considering that it requires a considerable portion of the kier boiling cycle to attain maximum operating pressure and that the maximum operating pressures and temperatures are usually less than those mentioned, I would expect that both factors are responsible for the excellence of the results reported to us. I would prefer that Mr. Bell tell you of the practical aspects of its use.

Mr. Bell: All I can say is that quite a few plants are using it in kier boiling and they put it in at the start.

Mr. Smith: The effect of Calgon is probably to remove lime soaps and other calcium and magnesium deposits at the start of the operation, after which the effect of reversion would be of little importance.

Mr. Barnard: Nothing has been said about the use of Calgon as an assistant in the dye bath. Have you any suggestions?

Mr. Smith: Calgon has been used as a dyeing assistant.

Mr. Bell: Mills that have had trouble, with scum and sludge, have put Calgon into the dye bath and it seems to have cut all that sludge, etc. In wool dyeing where the sludge is thick, it often filters out on the goods. Calgon dissolves all those thick oils and the various results of the impurities and hardness in the water and the goods, and in removing all that gum which resists penetration of the dyes, the stock comes out clearer. This is especially true when dyeing in Franklins and other types of pressure machines. You can tell with a microscope if it has been dyed with or without Calgon. Wool dyed without Calgon holds dirt and loosely attached dyestuff and oil, and, when Calgon is put in the bath, that stuff stays in the solution and drains off with the liquor.

Mr. Putnam: Has any effect of the Calgon been noticed on the dyestuff? Is the dyestuff itself affected?

Mr. Bell: Yes. Generally it makes the dyes faster to light. Calgon also makes some of the dyes more powerful, and it goes so far as to make some of the dull dyes into much bloomier colors. In plants that are using it, we have asked them if they have observed any detrimental color change on their regular dyes and their answer has always been "No". But, usually the mill is using dyestuffs that aren't sensitive to the particular metals from which their machines are fabricated, and they don't observe any particular change, generally only a brightening. We have several customers dyeing wool in iron Franklin machines. They all report an increase in brightness when Calgon is used. Duller shades would only be the result when poorly chosen dyestuffs are used in the machine.

Question: Does Calgon have a tendency to strip chrome on a chrome bottom?

Mr. Smith: I can't answer that on a basis of laboratory

observation. We haven't defined a chromium-Calgon complex. Certain indications of interest in dyeing operations that we have, tend to show that such a complex exists. We are interested in processes in which chromium is used, but so far have not done any quantitative work applicable to textiles.

Mr. Bell: The results indicate that some of the chrome may be taken off but with an excess of chrome present, as is usually the case, it does not affect the shade, and it does decrease crocking. That is because it cleans the wool better, I think.

Question: Is there any difference between the composition of the ice form and the glass form?

Mr. Smith: There is a slight difference between the flake form and the solid form. In a 25-pound bag of adjusted Calgon there are 23 pounds 10 ounces of glass, and 1 pound 6 ounces of mixed sodium carbonate and bicarbonate, the glass containing 90% sodium metaphosphate. The remaining 10% is tetra sodium pyrophosphate, which is effective in tying up magnesium but not effective on calcium.

The flakes contain approximately 5% pyrophosphate and 95% metaphosphate and are adjusted by the use of about 8 pounds of soda ash for 92 pounds of flakes. This gives the desired buffering action to impart to a ¼% solution a pH value of approximately 8.5. Such adjustment is particularly desirable in the flake form as the flakes are quite commonly used with soap, and unless the flakes are adjusted the soap does not lather effectively.

The pH value of 8.5 is less than the pH value of soap solutions, such as are used in contact with the skin. The solutions obtained in the domestic use of neutral soap are usually more alkaline than pH 9, and at certain concentrations may reach pH 10.

Question: I understand that in the flake form it is not available yet.

Mr. Smith: The first commercial unit went into operation this week. We have had a small scale unit in operation prior to this. It is hoped that within eight weeks we will have small containers of flake Calgon for distribution to the textile trade, dry cleaners and the like.

Mr. Healy: What form do you recommend to use in an acid dye bath?

Mr. Smith: The unadjusted form is that which is usually supplied for textile operations. Where a laundry operator prefers to buy it adjusted in the bag, the textile operator prefers the unadjusted material.

Question: How much would you recommend be used in an acid dye bath?

Mr. Bell: It varies with the nature of the goods and the water. If it is an open machine or a pressure machine, it would vary, but usually we find out by trial. We add one-half a pint of the standard solution for each 100 gals. in the dye bath, and see if it shows an improvement. If you don't think it is enough, you can double it, or maybe half as much will prove enough. Textile people use 2½ lbs. of dry Calgon plus a gallon of water to make the standard solution.

Question: Is the same quantity used for an ordinary dye bath?

Mr. Bell: That is generally the right procedure for all dyeing or scouring. Bear in mind that in continuous machines with their standing baths, additional Calgon must be added from time to time to take care of hardness introduced by the goods. In bleaching, we have good results down to ¼ pt., but generally it is ½ or ¾ pt. per 100 gallon. It is also used in acid piece dyes to eliminate cloudy results. Some mills use it in the wet finishing and don't put it in the dye bath at all. I think it is better to find the source of your trouble and use it there. It is in the wet finishing where we tackle many of the dye house problems. Some piece goods mills use it regularly, in both the washers and the dye kettles, as they find that it is distinctly beneficial even in the dyeing of thoroughly clean goods.

Question: How do you use this material in scouring pulled wool?

Mr. Bell: There is a lot of argument there. We have had good results on it. We are working on that now and have obtained a lot of very interesting results thus far, but do not feel prepared to give detailed instructions just at present.

Question: You say it hasn't been effective in removing aluminum.

Mr. Smith: It takes considerably more Calgon to dissolve a given amount of aluminum compound than it does to dissolve an equivalent quantity of calcium compound. It is a matter of economics as to whether the use of the complex phosphates are commercially practicable for this purpose. We have not yet been able to establish in the laboratory a rational mechanism for the effect of Calgon solutions on insoluble soaps of the trivalent metals.

Question: How about in the kier boiling, would pyrophosphate be more stable?

Mr. Smith: Sodium pyrophosphate would be more stable than sodium metaphosphate in kier boiling, but I see no reason for its use. Since sodium pyrophosphate is not effective for these purposes at ordinary temperatures I see no reason for believing it would be effective, even if stable, at temperatures of 240 to 250°.

Mr. Wilson: Have you tried preparing an aluminum stearate solution with Calgon?

Mr. Bell: We have had some success in removing aluminum soap, but we have done it mostly on the acid side; we haven't any real laboratory results on that, but we have had practical results. We treated piece goods with Calgon and acid. I believe the best results were obtained by scouring after that and then they dyed per-

fectly level. Previous to that hydrochloric acid and many reagents had been tried on these goods without success.

Mr. Smith: A strong metaphosphate solution very thoroughly wets aluminum stearate.

Question: I am going to ask if you have had any experience with Calgon in peroxide bleaching of raw wool? Did it have any stabilizing effect?

Mr. Bell: From personal observation, I am convinced that it did. (To Mr. Smith: "Have you had results from that in Pittsburgh?") From what I have seen in practice we got a better white and sometimes we thought we had cut down the time, but we haven't straightened it out thoroughly.

Question: What can you say as to the penetrating effect on fibers and textiles?

Mr. Smith: The high penetrative effect of solutions of Calgon has been a subject of considerable speculation. We have evidence of increased penetration even in heavy felts. We believe that in these cases the metaphosphate has increased penetration by dissolving and removing the lime soaps. When Dr. Gilmore's work is complete, we will be able to say definitely whether or not this is the cause.

Question: Is Calgon a good emulsifier?

Mr. Smith: Against normal oils and used alone, it is not effective. In the presence of soap or other special emulsifying agents, the Calgon is of advantage, particularly when they are diluted in hard water.

Mr. Nutting: In connection with the peroxide bleach bath, it is common practice to use lead coils for heating and I have seen some evidence that leads me to believe that Calgon may have some effect on metallic lead in the peroxide bath catalytically causing spontaneous decomposition.

Mr. Smith: Calgon forms a soluble complex with lead salts. The concentrations in which it is used are not such as to increase the rate of dissolving iron, Monel and brass and the like, but I can't say definitely that the concentration is insufficient to affect lead. There is reason to believe that it would not be.

Question: I'd like to ask one question. Is it better to add the Calgon in soaping operations or should it be boiled in with the soap? Should it be added in the rinsing or in the washing operation after the soap and is it possible to use less carbonate?

Mr. Bell: Calgon has been used all those ways. Some mills make it up into their soft stock soap, adding it at the time that they run in the cold water, after the soap and alkali have been boiled sufficiently. We do not particularly recommend this method. You get practically the same results by handling it in solution. It is very convenient usually, to have it in one big supply tub, and smaller wooden buckets. Set a bucket by each washer and measure it out with a dipper as you want it. In the dyeing operations, when you are using soda ash for softening the water, not for alkalinity, you could eliminate soda ash entirely. Calgon isn't an alkali. If you need alkali for its detergent properties, I wouldn't recommend cutting it at all.

Question: Doesn't it have a tendency to give too much alkalinity for the skin?

Mr. Smith: No. Decidedly not. Soap used in contact with the flesh has a higher pH value than that of Calgonized water alone. The pH value of solutions of soap in Calgonized water is less than a solution of soap in ordinary water. The use of Calgonized water with soap would, therefore, be easier on the skin than the use of soap in ordinary water. Either with or without soap the alkalinity of Calgon solutions is markedly less than that of the common water softening chemicals, such as trisodium phosphate and soda ash, used as household detergent aids.

Mr. Grady: I wonder how your work has been done on Calgon eliminating the crocking. Just acid colors you know.

Mr. Bell: The stock is cleaner and therefore dyes better and crocks less. It is a case of getting the stock clean.

Mr. Grady: How about scouring after they were dyed?

Mr. Bell: Scouring after they are dyed usually eliminates crocking anyway.

Mr. Lane: Take a heavy wool using 8 to 10% of acid black. The same is true of maroons and dark shades. Does the Calgon help the crocking?

Mr. Bell: Yes, because it keeps the dyes in perfect condition and it also removes the dirt, which is the main cause of crocking with a good dyestuff.

MEETING OF SOUTH CENTRAL SECTION

THE South Central Section held its spring meeting at the Read House in Chattanooga, Tenn., on May 5th, 1934.

The speakers for the evening were, Walter E. Hadley, on his experience with stones, and Paul Bolen of the Dissenoff Chemical Co., Savannah, Ga. An entertaining programme was enjoyed by about 25 members and guests. Chairman Harold Schroeder presided.

The next meeting will be a joint session of the Southern and the South Central section to be held in Chattanooga in the late summer.

Respectfully submitted,

H. BRUCE KIMBELL, *Sec'y.*

Proceedings of the American Association of Textile Chemists and Colorists

The Iodine Number of Wool:

A Method for Determining the Action of Various Chemical Reagents on Wool and Other Proteins

By MILTON HARRIS, HARVEY NEVILLE and WILLIAM C. FRITZ*

* The experimental part of this research was done by William C. Fritz, Eavenson and Levering, Research Fellow at Lehigh University. The work was directed by Harvey A. Neville, Associate Professor of Chemistry at Lehigh University, and Milton Harris, Research Associate at the Bureau of Standards from the American Association of Textile Chemists and Colorists. The latter's contribution to this study forms a part of the study of wool being undertaken by the Association on a grant from the Textile Foundation.

The purpose of this research was to find a method for determining the action of various chemical reagents upon wool. The iodine number provides a quantitative measure of the extent to which the amino groups are affected by various treatments of the protein.

Amino acids and proteins exhibit iodine numbers as determined by the standard method. The iodine numbers of such substances do not indicate ordinary unsaturation but are shown to be related to the free amino nitrogen content.

The iodine numbers of some typical proteins are reported and a general correspondence between the iodine numbers and the isoelectric points of the proteins is shown.

Conversion of amino groups to hydroxyl groups, combination of amino groups with strong acids, and other chemical reactions which affect the amino groups reduce the iodine numbers of amino acids (with the exception of cysteine) to zero.

Part of the iodine number of wool is shown to be due to cysteine which is very susceptible to oxidation. The iodine number of wool is therefore affected by reactions of chemical reagents with the amino or the cysteine groups.

This method will distinguish, for example, between reversibly adsorbed and chemically combined acid. The latter can be removed by the action of an alkali and this restores the original iodine number of the wool.

I. Introduction

THE term "iodine number" is ordinarily associated with oils and fats for which it serves as a measure of chemical unsaturation. It represents the number of centigrams of iodine which combine with one gram of material.

The aliphatic amino acids are saturated compounds, but they nevertheless exhibit definite and reproducible iodine numbers which may be determined by the same methods as those used for fats and oils. The experimental evidence indicates that the iodine reacts only with the free amino groups in these compounds, unless, like cysteine, for example, they contain readily oxidizable groups which also react.

The iodine numbers of proteins may be determined by the same method used for oils and a part, at least, of the iodine number of each protein may be attributed to the free amino groups. This provides a useful means of determining the extent to which these groups are affected by various treatments of the protein.

This paper is a report of a brief survey on the use of this method for studying the action of various chemical reagents upon wool.

II. Methods

The iodine numbers reported here were obtained by a slight modification of the standard Wijs method[1], using a solution of iodine monochloride in glacial acetic acid, which was 0.1 normal with respect to total halogen. Samples of the amino acids or their derivatives weighing about 0.1 gram and of the proteins weighing about 0.5 grams were used for each determination.

The wool fibers were prepared by cutting them into very short lengths. The iodine number of the cut fibers was identical with that obtained from powdered wool. All samples were conditioned at a relative humidity of 65 per cent (70° F.), conditioned and dried samples gave the same iodine number calculated on the basis of the wool protein.

The determinations of iodine numbers were carried out as follows: a weighed sample was placed in a flask and 25 ml. of glacial acetic acid was added. Twenty-five ml. of Wijs solution was added and the mixture was allowed to stand, with occasional shaking, for one-half hour at 25° C. At the end of this time, 50 ml. of water and 20 ml. of a 15 per cent solution of potassium iodide were added. Sodium thiosulfate solution was then added in an amount equal to that required by a blank determination. After the solution had stood for one-half hour, 10 ml. of

[1] Methods of Analysis of the Association of Official Agricultural Chemists, 3rd Edition, p. 73.

a 1 per cent starch solution was added and the excess of thiosulfate was titrated with a standard iodine solution. This modification, namely, the addition of excess thiosulfate and reverse titration with iodine, was used in all of the determinations of iodine numbers. By this procedure all of the iodine was removed from the wool fibers and the wool appeared as white as the original sample.

Analyses of wool samples which had been used for iodine number determinations showed that no chlorine or iodine remained in combination with the wool after the thiosulfate treatment. This indicates that the halogen which combined with the wool in the Wijs solution was removed by the aqueous solutions in some combined form and not as free iodine, since it did not react with its equivalent of thiosulfate.

III. Results and Discussion

1. *Amino Acids and Derivatives*:— The iodine numbers of a few amino acids and derivatives determined by the above method are recorded in Table 1.

Table 1.

The iodine numbers of a few amino acids and derivatives:

Compounds	Iodine Number
Glycine—CH_2NH_2COOH	15.5
Glycollic acid—$CH_2OHCOOH$	0
Glycine hydrochloride—$CH_2NH_3COOH.HCl$—	0
Leucine—$CH_3(CH_2)_3CHNH_2COOH$	20.6
Acetamide—CH_3CONH_2—	0
Diethylformamide—$HCON\ (C_2H_5)_2$—	0
Urea—$CO\ (NH_2)_2$—	0
Cysteine hydrochloride—$CH_2SHCHNH_2COOH.HCl$	89.
Hippuric acid—$C_6H_5CONHCH_2COOH$	0

A simple amino acid such as glycine gives an iodine number while the corresponding hydroxy acid does not react with iodine and gives no iodine number. Further evidence that the iodine reacts only with the free amino group is offered by the fact that acid salts of the amino acids, such as the hydrochloride, likewise give no iodine number. However, the reaction of halogen with the simple amino acids is by no means complete under the conditions of these experiments since the theoretical iodine numbers of glycine and leucine, assuming a stoichiometric reaction, would be 338 and 194, respectively. It is obvious that the study of other factors such as pH values and molecular concentrations are necessary if this method is to be made strictly quantitative. As the molecular weight of the amino acid increases, the reaction with iodine becomes more nearly complete and as will be shown, it is approximately stoichiometric for some of the proteins.

The hydrochloride of cysteine should give a zero iodine number if the reactions were limited to free amino groups. However, this particular amino acid contains the easily oxidizable —SH group which reacts with iodine to produce cystine. The theoretical iodine number of cysteine hydrochloride corresponding to the reaction $2\ R.CH_2SH + I_2 = R.CH_2S—SCH_2.R + 2HI$ is 83. The value given in Table 1 is in fairly good agreement in view of the difficulties attending the use of this reaction for the quantitative estimation of cysteine as reported by Lucas and King[2].

Since acetamide, hippuric acid and similar amides give no iodine numbers, it may be concluded that the amide nitrogen does not contribute to the iodine number of a protein.

Reaction of iodine with the amino group may involve either an addition or an oxidation reaction. It may be assumed by analogy that the addition of iodine (or chlorine) from the Wijs solution occurs at the amino group in a manner similar to the addition of hydrochloric acid. The mode of combination of acids with amino groups has recently been discussed by Phillips[3] who represents the chlorine or other anion as bound to the molecule through an atom of hydrogen having four electrons in its shell. A similar structure may be used to represent the combination of the amino group with two halogen atoms instead of with hydrochloric acid.

Since the Wijs solution is also an oxidizing agent, it is possible that the amino group has been at least partially oxidized during the iodine number determination[4].

2. *Proteins*:—In Table 2 are recorded the iodine numbers of some proteins. While it is not desired to place any emphasis upon iodine numbers as a means of comparing

Table 2.

The iodine numbers and isoelectric points of a few proteins:

Protein	Source	Isoelectric Point	Iodine Number
Fibroin	Degummed silk	2.5[5]	3.7
Keratin	Texas wool	3.4[6]	14.2
Gelatin	Knox, food	4.7[7]	10.2
Zein	Corn	6.2[8]	27.5
Gliadin	Wheat	6.5[8]	25.0

different proteins, a general relationship is evident. Fibroin which has a low content of free amino nitrogen and an isoelectric point at a relatively high acidity, has a low iodine number. On the basis of isoelectric points and the accepted values for free amino nitrogen, wool keratin should be next in order with an iodine number less than

[2] C. C. Lucas and E. J. King, The Iodimetric Titration of Cysteine and Allied Substances, Biochem Jour. vol. 26, p. 2076 (1932).

[3] H. Phillips, The Formation and Constitution of Protein Salts From the Standpoint of Modern Theories of Valency, J. Int. Soc. Leather Trade Chemists, vol. 17, pp. 151-165 (1933).

[4] A. P. Mathews, Physiological Chemistry, pp. 122-123 (1916) Wm. Wood & Company.

that of gelatin. The apparent inconsistency in Table 2 is readily explained by the fact that keratin is the only protein with an appreciable sulfur content, a portion of which is present as cysteine, which, as we have shown, reacts readily with iodine. Therefore, only a portion of the iodine number of wool is due to the amino nitrogen content of keratin. Zein and gliadin exhibit high iodine numbers and are reported to have isoelectric points at relatively high pH values.

The experimentally determined iodine numbers of silk, wool and gelatin are in fair agreement with the calculated values assuming stoichiometric reaction with the amino groups. These values are compared in Table 3. Zein[8] is reported to contain no free amino nitrogen and gliadin to contain only 1.9 mg. of amino nitrogen per gram of protein. For these the calculated iodine numbers are much lower than the experimental ones.

Table 3.

Comparison of the experimental iodine number with calculated iodine numbers assuming stoichiometric reaction with the amino groups:

Protein	Milligrams Amino Nitrogen per Gram Protein	Calculated Iodine Number	Experimental Iodine Number
Silk	1.5 to 1.7[9]	2.7 to 3.1	3.7
Wool	5.7[10]	10.3	8.3 to 9.4*
	9.2[11]	16.7	
Gelatin	5.5[12]	9.9	10.2
Zein	0 [12]	0	27.5
Gliadin	1.9[12]	3.4	25.0

*These are corrected values, obtained by subtracting that portion of the iodine number due to reaction with the cysteine group from the iodine number of untreated wool. Reference to table 4 shows that the action of nitrous acid or formaldehyde upon wool lowers the iodine number 8.3 to 9.4 units. Since these reagents may be presumed to react with the free amino groups but not with the cysteine sulphur, the portion of the iodine number of wool due to amino nitrogen appears to be of this order.

3. *Wool*:— Samples of raw wool were treated with various chemical reagents and their iodine numbers were determined with the result shown in Table 4.

A comparison of the iodine numbers in experiments 1 and 2 demonstrates that overscouring the wool, for example, by increasing the temperature and the concentration of alkali to such an extent that the wool is damaged in appearance and harshened, does not affect either the content of cysteine sulfur or of amino nitrogen.

In the neutral solution (experiment 4) hydrogen peroxide does not affect the iodine number. In the acid solution (experiment 6) peroxide has the same effect as that produced by the acid alone under the same conditions (experiment 5) and this effect is entirely removed by neutralization (experiment 7). In contrast, the alkaline peroxide solutions (experiments 8 and 9) lower the iodine number to a marked degree. These results indicate that in neutral and acid solutions hydrogen peroxide oxidizes neither the cysteine sulfur nor the amino groups in wool, while in alkaline solutions, hydrogen peroxide apparently attacks both groups to a limited extent.

Table 4.

Iodine numbers of raw wool and wool treated with various chemical reagents:

Experiment No.	Treatment	Iodine No.
1	Raw wool—scoured with solvents and rinsed.	14.2
2	Overscoured—1% soda ash, 70° C.	14.2
3	Formaldehyde, 1% solution	5.9
4	Neutral H_2O_2, 1% solution	14.1
5	NH_2SO_4	7.2
6	Acid H_2O_2, 1% solution NH_2SO_4	7.2
7	Treatment 5, followed by Na_2CO_3 solution	14.2
8	Ammoniacal H_2O_2, 1% solution	4.3
9	Alkaline H_2O_2, 1% solution (0.5% N_2CO_3)	5.3
10	Acid solution of $KMnO_4$, 1%, 8 hours	1.5
11	Solution HNO_2, 0.1%, 25° C.	4.7
12	Solution HNO_2, 0.1%, 0° C.	4.8

A strong oxidizing agent, potassium permanganate (experiment 10) lowers the iodine number to a greater degree than any other reagent used, but the wool is severely damaged by this treatment.

A solution of nitrous acid would be expected to lower the iodine number of wool by converting amino groups to hydroxyl groups. Nitrous acid may also oxidize the cysteine sulfur in wool. The iodine numbers in experiments 11 and 12 in Table 3 were obtained after 3 hours' treatment with 0.1 per cent solutions of nitrous acid. Higher concentrations or longer treatments do not produce appreciably lower iodine numbers, but cause an increased yellowing of the wool, especially at temperatures above 0° C.

While acid lowers the iodine number, as already pointed out, if it is removed by an alkaline treatment the iodine number returns to the original value. This complete neutralization or removal of combined acid is accomplished only by soaking the acid-treated wool for a considerable time in an execss of the alkaline solution. Merely titrating rapidly to the phenolphthalein end point does not re-

[5] M. Harris, The Isoelectric Point of Silk, B. S. Jour. Research, vol. 9, pp. 557-560 (1932).
[6] M. Harris, The Isoelectric Point of Wool, B. S. Jour. Research, vol. 8, pp. 779-786 (1932).
[7] L. Michaelis and Grineff. Naturwissenschaften, vol. 18, p. 447 (1930).
[8] F. A. Csonka, J. C. Murphy & D. B. Jones, The Isoelectric Points of Various Proteins, J. A. C. S., vol. 48, pp. 763-768 (1926).
[9] M. Harris—Unpublished report.
[10] Meunier and Rey, Sur less Proprietes de la Laine, J. Soc. Leather Trade Chemists, vol. 11, p. 508 (1927).
[11] J. B. Speakman and M. C. Hirst, The Constitution of the Keratin Molecule, Trans. of the Faraday Soc. vol. 29, pp. 148-164 (1933).
[12] D. D. Van Slyke & F. J. Birchard, J. Biol. Chem., vol. 16, p. 539 (1931).

move all of the combined acid. The evidence that a definite amount of acid combines chemically with wool and cannot be removed by mere rinsing with water is illustrated in Figure 1. Here it is shown that prolonged rinsing alone removes only a portion of the acid, while

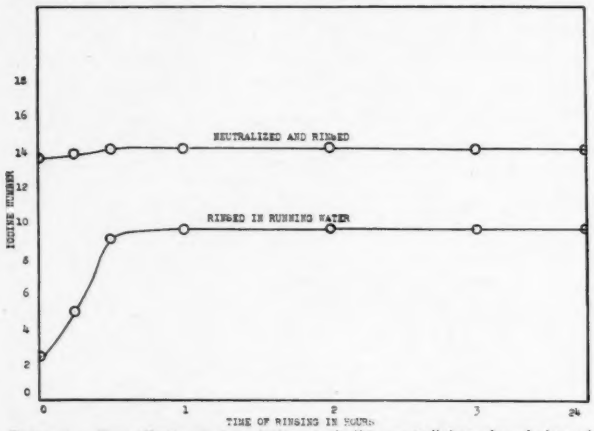

Figure 1. The effects of (a) rinsing, and (b) neutralizing plus rinsing of wool previously soaked in normal sulfuric acid, as shown by the iodine numbers.

all the acid remaining on the wool may be readily removed by neutralization after which the iodine number of the wool returns to its original value. Since it has been shown that the iodine number bears an inverse relationship to the amount of acid on the wool, the minimum difference between the curves may be taken as a measure of the chemically combined acid. The lower curve represents the effect on the iodine number produced by the amount of acid which is reversibly adsorbed, and the upper curve the similar effect of the total amount of acid held by the wool after neutralization.

It is well known that strong alkalis, even in very dilute solution, have an injurious action upon wool and that somewhat more concentrated solutions will destroy the wool fibers, dissolving or dispersing and hydrolyzing the keratin. Figure 2 illustrates the effects upon the iodine number and upon the amino nitrogen content of wool resulting from the action of 0.5 normal sodium hydroxide solution at 38° C. Separate one-gram samples of wool were treated with 100 ml. of 0.5 normal sodium hydroxide solution for each test. At the time intervals indicated two samples were neutralized with acetic acid. One was evaporated to dryness at 60° C. under reduced pressure and the iodine number of the residue was determined. The amino nitrogen content of the other sample was determined by the Van Slyke method. Although the wool fibers appear to be dissolved in the sodium hydroxide solution at the end of two hours, the results of the Van Slyke analysis show that only partial hydrolysis of the wool has been accomplished even at the end of thirty-six hours. The iodine number rises rapidly during the first hour and becomes constant after 8 hours. The results show that the determination of the iodine number is not a measure of the hydrolytic breakdown of wool.

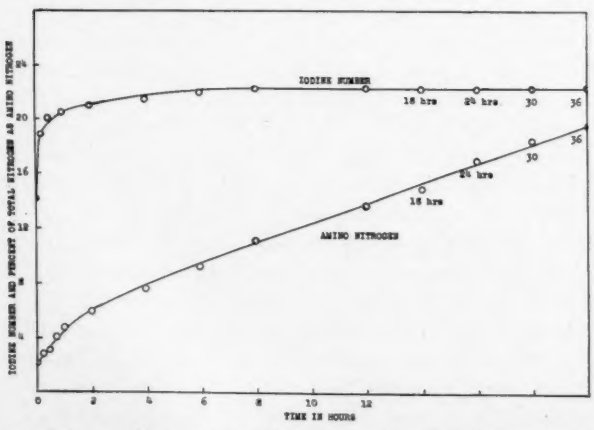

Figure 2. The effects upon the iodine number and free amino nitrogen content of wool produced by continued action of 0.5 normal sodium hydroxide solution at 38° C.

The examples and suggestions given above show the applicability of the method for a number of purposes. Further study may increase the accuracy and utility of the method.

MEETING OF PIEDMONT SECTION

THE second quarterly meeting—of the Piedmont Section of the A. A. T. C. & C. was held on Saturday, May 19th, at the Poinsett Hotel in Greenville, S. C.

About eighty-five members and friends sat down for the banquet which was served promptly at 7:00 P. M.

Following the banquet, for the technical part of the program, the following papers were presented:

"Sulfonated Oils——Theory and Practice", by Alfred R. Macormac, chief chemist of the Chemical Products Co., Greensboro, N. C.

"A Theory of Dyeing", by Harold Schroeder, chairman of the South Central Section and also chemist and dyer for the Dixie Mercerizing Co., Chattanooga, Tenn.

"Some Milestones in the Chemistry of Textile Processing", by Dr. Eugene R. Manning, head of the Chemistry and Dyeing Dept., Clemson College, Clemson, S. C.

A very entertaining program was presented by the local entertainment committee. Plans for the Summer outing were discussed. It was decided to hold the summer outing at Mayview Manor, Blowing Rock, N. C., on Saturday, June 30th.

All members and friends who are planning to attend this outing should write to Mayview Manor immediately to make reservations, because a very large attendance is expected.

Respectfully submitted,

JOHN C. ROBERTSON, *Secretary.*

NINETY-FIFTH COUNCIL MEETING

THE Council held its 95th meeting at the Chemists' Club of New York, on Friday afternoon, May 11th. President Robert E. Rose presided. Also present were: William R. Moorhouse, Treasurer; Louis A. Olney, Chairman of the Research Committee; J. F. X. Harold, Donald H. Powers, Carl Z. Draves, William D. Appel, and Hugh Christison, Councilors at Large; Heyward F. Lawton, representing Rhode Island; Hans Meyer, representing New York, and Harold C. Chapin, Secretary.

The minutes of the last meeting were approved as published. The Treasurer's report of May 9th and the Secretary's balance sheet of May 10th, both attached hereto, were accepted.

Each of the following was elected to the class of membership specified, as of thirty days from publication of application, provided that no objection be received before that date by the Secretary.

Active

H. D. Boswell, Miles A. Dahlen, Herbert P. Ford, Marion E. Griffith, Nelson W. Humbaugh, Clifford Jones, Frank Korman, Otto W. Leibiger, Charles E. Lennox, Alexander C. Mackey, Alfred Marsh, J. Ernest Meili, Harry L. Miller, Clarence E. Moss, Albert L. Mulcahey, Frank S. Pittman, A. E. Raimo, R. M. Ritter, Robert Schmeidler, John R. Senior, Paul B. Seydel, Edward J. Siegrist, H. Gillespie Smith, Alan F. Thompson, R. B. Weatherston.

Junior

Talbot Barnhill, William R. Howes, W. F. Uhlig.

Associate

Philip S. Bolton, L. L. Griffiths, Jr., L. W. Neal, George W. Shearon.

Student

L. R. Ellenburg, E. E. Flowers, G. M. Kidder, Harold Smith, G. R. Thompson, W. J. Wynn, Jr.

Virgil T. Hartquist and Alfred C. Stacey were transferred from Junior to Active membership.

It was reported that there were 1253 members of all classes in good standing, which was 138 more than at the same time last year; and that 150 members had been elected or re-instated since November first, the beginning of the fiscal year.

It was voted that in reciprocation for similar courtesies the regular publications of the Association be mailed as issued to the Federation Internationale des Associations des Chimistes du Textile et de la Couleur.

An appropriation of $8,100 from the Textile Foundation was accepted and voted to research projects as planned at the last previous Research Committee meeting.

It was suggested that many ex-members of the Association might reinstate themselves if informed regarding procedure. The Secretary therefore undertook to remind each Section Chairman of the provision in the Constitution regarding this; and its interpretation by the Council that an ex-member dropped on May first of any year can reinstate himself in a subsequent year by payment of $2.50 plus current dues of $5.00. The Constitution permits reinstatement of a member in the fiscal year in which he is dropped, upon payment of dues for that year only; and reinstatement of a member resigning on November first of any year, upon payment of current dues only, in any succeeding year.

It was arranged that the next Council meeting be at the Engineers' Club of Boston, on Friday afternoon, June 15th.

Respectfully submitted,

HAROLD C. CHAPIN, *Secretary.*

Treasurer's Report

MAY 9, 1934

General Fund

Cash on hand—March 20, 1934 (Date of last Report)		$9,924.60
Receipts—March 20, 1934 to May 9, 1934		987.51
		$10,912.11
Expenditures—March 20, 1934, to May 9, 1934	$338.42	
Transferred to Research Fund March 23, 1934	2,000.00	2,338.42
Balance—May 9, 1934		$8,573.69

Research Fund

Cash on hand—March 20, 1934 (Date of last Report)	$1,807.05
Receipts—March 20, 1934 to May 9, 1934	77.00
Transferred from General Fund March 23, 1934	2,000.00
	$3,884.05
Expenditures—March 20, 1934 to May 9, 1934	1,807.60
Balance—May 9, 1934	$2,076.45

Bank Balance, May 9, 1934

General Fund	$8,573.69
Research Fund	2,076.45
	$10,650.14
First National Bank—Checking Account	$5,113.71
First National Bank—Savings Account	5,536.43
	$10,650.14
Total of Checking and Savings Accounts November 1, 1934	$9,014.60
Total Receipts—November 1, 1933 to May 9, 1934	
General Fund:	

From Secretaries	$6,478.35		
From Members	10.00	$6,488.35	
Research Fund:			
From Secretaries	$1,707.00		
From Textile Foundation	2,150.00	3,857.00	$10,345.35
			$19,359.95

Total Expenditures—November 1, 1933 to May 9, 1934		
General Fund	$3,311.28	
Research Fund	5,398.53	8,709.81
Total of Checking and Savings Accounts May 9, 1934.....		$10,650.14

Respectfully submitted,
W. R. MOORHOUSE, *Treasurer.*

Secretary's Balance Sheet

MAY 10, 1934

	Applications	Dues, regular & reinstatement	Dues, sustaining & contributions	Dues Corporate	Miscellaneous	Totals
Received by both Secretaries, Nov. 1 to Mar. 21	$400.00	$4,620.51	$255.00	$1,500.00	$133.50	$6,909.01
Received by Secretary, Mar. 21 to May 10.....	132.50	798.24	20.00	.....	149.19*	1,099.93
Receipts, total for fiscal year to May 10.....	532.50	5,418.75	275.00	1,500.00	282.69	8,008.94
Transmitted to Treasurer by both Secretaries..	475.00	5,121.81	275.00	1,500.00	230.25	7,602.06
Leaving to order of Secretary in Appleton Bank of Lowell	57.50	296.94	.....	.....	52.44	406.88

*Anal. Meth. & Postage.....	$17.41
Year Books	6.00
Light Fast. Reports.....	10.78
Silk Standards	2.00
Launderometer Royalties	77.00
Knit tubing	36.00
	$149.19

EIGHTY-EIGHTH RESEARCH COMMITTEE MEETING

THE 88th Research Committee meeting followed the Council meeting at the Chemists' Club of New York, on Friday afternoon, May 11th. Present were Louis A. Olney presiding, W. D. Appel, P. J. Ariente, J. R. Bonnar, W. H. Cady, H. M. Chase, Hugh Christison, H. D. Clayton, C. Z. Draves, E. Freedman, J. F. X. Harold, Ralph Hart, B. L. Hathorne, F. Krassner, H. F. Lawton, Hans Meyer, W. R. Moorhouse, G. A. Moran, H. A. Neville, R. E. Rose, and H. C. Chapin.

It was reported that the American Standards Association, requested by the British association to give data on concentration tests for dyes, had applied to us for assistance, and had been informed that we had established no standard tests for dye concentrations. The opinion was expressed that this was primarily a function of the dye manufacturers.

A letter was received from Professor H. E. Shiver, advocating greater publicity regarding the necessity of routine textile testing. It seemed the opinion of the Committee that such publicity was one of the ends of the Association, toward which much progress had been made already.

It was announced that the Atlas Electric Devices Co. was issuing a new bulletin on the Launderometer, with new prices; and would be glad to mail a copy to any member requesting it.

Dr. Draves submitted a report from the committee on the list of chemical specialties for the Year Book.

Mr. Hathorne reported on the research plans of the Rayon Committee.

Dr. Harold suggested a committee to confer with other associations on unification of standards, and was supported by Mr. Appel. Dr. Draves considered this more properly a function of the various sub-committees, with regard to the standards on which they themselves were working. Mr. Clayton reported progress in this direction by the sub-committee on Shrinkage of Textiles, stating that the Federal Specifications Board and Committee D 13 of the American Society for Testing Materials had adopted our method for determining shrinkage of cotton fabrics. Mr. Freedman had confirmation of this in a letter from Professor Ball of Committee D 13 approving uniform specifications for shrinkage of three classes.

On motion of Mr. Cady it was voted that for detailed planning of the research program of the Association there be established a sub-committee to consist of the Chairman of the Research Committee, the chairman of each committee advisory to a Research Associate, and such other members as the Chairman should appoint.

Respectfully submitted,
HAROLD C. CHAPIN, *Secretary.*

AMERICAN
DYESTUFF
REPORTER

LOUIS A. OLNEY, Sc.D.
Professor of Chemistry and Dyeing, Lowell Textile Institute
Directing Editor

NORMAN A. JOHNSON
Managing Editor

MYRON DREW REESER
Advertising Manager

Published biweekly by
HOWES PUBLISHING CO., INC.
440 Fourth Avenue, New York City

A. P. HOWES, President
M. D. REESER, Secretary
H. F. CRAWFORD, Treasurer

Subscription price: $5.00 per year; Canadian $6.80; foreign $6.00

Vol. XXIII June 4, 1934 No. 12

HERMAN A. METZ

WE HARDLY feel qualified to comment upon the passing of General Herman A. Metz. After the wide and active career which filled his life for the past sixty-six years it is difficult to realize that this person has passed on, leaving as he does a tremendous void in the hearts of those who knew him. And to those who worked with him the emptiness is much more real as is expressed in the words of one who had the privilege of daily contact with him: "All who knew him will miss him, but to those of us who actually worked with him his place can never be fully taken." His career was one that touched all phases of life—political, social and economic.

He was born in New York City on October 19, 1867, and after his schooling he entered the employ of P. Schulze-Berge as an office boy in 1881. In 1893, after constant advancement he became the vice-president and general manager of this company, and in 1899 he was its majority stockholder and president. Through various consolidations and changes the firm name had, in the meanwhile, become Victor Koehl & Co.

In 1903 the chemical and dyestuff department was separated from the pharmaceutical branch of the business and incorporated as H. A. Metz & Co., the manufacture of color and chemicals being carried on by the Consolidated Color & Chemical Co., of which Mr. Metz was president. In addition he became president of the H. A. Metz Laboratories, Inc., Ettrick Mills, Textileather Company, New York and Hanseatic Corp., and also served as a director in a number of banks.

In July, 1926, his dyestuff selling interests were turned into a new concern, the General Dyestuff Corporation, of which he became president. At the time of his death he was chairman of the Board of Directors of this corporation.

His life was not entirely spent in industrial pursuits as is shown by his other activities. At various times he was Comptroller of the City of New York, a member of Congress, a member of the Board of Education of Brooklyn and New York City, a member of the State Board of Charities, a director of the Interborough Rapid Transit Co., acting for the public, a colonel and ordnance officer of both the New York National Guard and the United States Army Reserve Corps and on the eve of his retirement in 1931, he was elevated to the post of brigadier general. Further, he was a member of a great many chemical and industrial societies, he was honored with the degree of Sc.D. from Union College and the degree of LL.D. from Manhattan College. He founded the Kings County Democratic Club in Brooklyn and was president of the National Civic Club. He was also a governor of the Democratic and Reform Club of New York and served as a member of both the Hughes and Miller charter revision committees.

Here was a man whose activities speak for themselves. It is impossible for us to add much more to this. "His was a life of singular achievement and the 'footprints in the sand of time' left by this man who recognized no defeat, are standards of accomplishment to which all who knew him may reverently aspire."

It is only with regret that we can speak of his passing and we know that it is only with regret that others can think of his death. Whatever we can say or do now can not detract from the personality of this man who played so prominent a part in the dyestuff industry of this country and led him to be honored and respected by all. The dyestuff and chemical industry, in losing Mr. Metz, has lost one of its outstanding figures for all time.

Recent Developments in the Chemistry of Silk and of Silk Processing--III

(Continued from page 303, May 21st issue)

By WALTER M. SCOTT, Ph.D.
Gustavus J. Esselen, Inc., Boston, Mass.

CHAPTER IV
THE WEIGHTING OF SILK

AN earlier paper by the writer (Am. Dyestuff Reptr. *20*, 517) reviewed in some detail the developments which had taken place in this field prior to the year 1931. Therefore it will be only necessary at this time to outline the further progress since that date.

The Normal Tin Weighting Procedure

In order to discuss intelligently the suggested additions and substitutions, it is advisable to first list in chronological order the various steps in the procedure which has for many years been commonly used for the weighting of silk skeins or silk pieces with compounds of tin. This procedure is as follows:

1. Immersion in a solution of stannic chloride whose gravity is not over 30° Be. and whose temperature is about 60° F. A preliminary treatment in a dilute acid solution may be given if desired.
2. Removal of the surplus tin solution by whizzing.
3. Thorough washing with cold water in order to completely hydrolyze the stannic chloride which is absorbed by the fibers.
4. Immersion in a solution of disodium phosphate whose gravity is not over 6° Be. and whose temperature is about 140° F.
5. Washing with cold water to remove the surplus phosphate solution.
6. Repetition of steps 1 to 5 up to four or five times as desired.
7. Immersion in a solution of sodium silicate whose gravity is not over 5° Be. and whose temperature is about 140° F.
8. Washing with cold water to remove the surplus silicate solution.

Additions to the Stannic Chloride Solution

1. Sodium Chloride—A recent patent claims that if the stannic chloride is dissolved in a saturated solution of common salt, a much lower concentration of tin can be used. This solution provides a quick exhaustion of the tin, and there is subsequently very little loss of surplus tin in the wash water.

2. Cerium Acetate—This compound has been mentioned as being suitable to add to the stannic chloride weighting solution. Zinc chloride may also be added to the above mixture if desired.

3. Metallic Carbonates—The stannic chloride solution is deacidified by the addition of the carbonate of a metal whose chloride is soluble and whose phosphate is insoluble. Lithium, barium, calcium, magnesium, iron, chromium, lead, bismuth, etc. are considered suitable. It is claimed that a clear and very stable weighting solution may be prepared in this manner. The silk takes up weight faster than normal in such a solution and there is less injury to the silk during the process. The usual fixation with disodium phosphate follows the tin treatment.

4. Rare Earth Carbonates—The carbonates of rare earth metals such as lanthanum, didymium, thorium, etc., may be used alone or in mixture to deacidify the tin weighting solution.

5. Sulfocyanates—Ammonium sulfocyanate is added to a very concentrated solution of stannic chloride. Barium sulfocyanate may be used if desired in conjunction with the ammonium sulfocyanate. Silk is padded with this weighting solution, aged for several hours, padded with a 30 per cent solution of trisodium phosphate, aged and dried. It is claimed that considerable time is saved by this special weighting procedure.

Modifications of the Phosphate Fixing Bath

1. Diammonium phosphate is suggested as a substitute for disodium phosphate.

2. After the treatment with stannic chloride it is proposed to immerse the silk in a solution of phosphoric acid before the fixation with disodium phosphate.

3. Disodium phosphate, phosphoric acid and magnesium chloride may be added directly to the stannic chloride solution in such proportions that the pH is kept between 0.8 and 2.1. After immersion in this solution, the silk is passed without washing into a fixing bath containing disodium phosphate, ammonia and urea. A subsequent treatment may be given in a dilute alkaline solution of neutral resins or resin-like condensation products.

Recovery of Tin from the Phosphate Bath

It has been found that the tin which was carried over

into the phosphate fixing bath, can be almost quantitatively removed by passing the waste phosphate solution through a filter charged with active aluminum hydroxide. The filter is subsequently washed with a solvent for tin, such as a solution of sulfur and sodium sulfide.

The Clavel Process

The early developments sponsored by Rene Clavel were described in the earlier paper by the author, mentioned at the beginning of this chapter. Since that time the procedure has been modified by subsequent patents until a completely continuous process for weighting silk piece goods has been evolved. This process, in brief, is as follows:

The silk is first made more receptive for the tin by a pre-treatment in strong formic acid, or in a 26 per cent solution of hydrochloric acid, using a protective colloid if necessary. After squeezing out the excess of acid, the following operations are carried out in succession:

1. Passage through an initial tin solution followed by a light squeeze and a 2-minute ageing in the air.
2. Passage through a second tin solution followed by a light squeeze, a 2-minute ageing, and a heavy squeeze.
3. Passage through a cold solution of monosodium phosphate, followed by the usual squeezing and ageing.
4. Passage through continuously changing wash water and through fresh water sprays followed by a squeeze.
5. Passage through a solution of disodium phosphate at 60° C. followed by a wash and a squeeze.

This entire cycle is repeated as many times as desired and then the silk may be finished in the usual silicate bath.

Clavel claims that in certain cases, practically all the operations mentioned above may be combined into one. For example, the silk is immersed in a bath containing stannic chloride, formic acid, sodium silicate, sodium phosphate and glue, and then transferred to a fixing bath containing ammonium carbonate.

A further innovation is to thicken a weighting solution similar to the above with gum arabic or dextrin, and pad this paste on one or both faces of the silk, or apply it in a pattern by means of an engraved roller. Novel effects may be produced by this procedure.

Lead Weighting

Within the last few years lead has gained a firm foothold in the silk manufacturing world as an adjunct to the usual tin weighting procedure. After one or two cycles of alternate tin and phosphate treatments, the silk is acidified with dilute acetic acid and then treated immediately with a solution of lead acetate, followed by the usual fixation with disodium phosphate. This lead-phosphate cycle may be repeated as desired but in each case the silk must be acidified with acetic acid before immersion in the lead acetate solution.

Recent patents claim that sodium or potassium borate, silicate or tungstate may be substituted in place of sodium phosphate as a fixing agent for the lead. Also that lead chloride may be used in place of lead acetate. In this case, after weighting with tin and phosphate the silk is treated in an aqueous solution containing sodium acetate and isopropylated B-naphthylate disulfonic acid, then with lead chloride in the presence of phosphoric acid, disodium phosphate, or trisodium phosphate, and finally with a solution of ammonium carbonate.

Some concern has been felt as to the possible health hazard of lead-weighted silk. A careful study of this subject was recently made by Fairhall and Heim of the Harvard Medical School. They found that no more than the faintest trace of lead, which could be detected only by microchemical methods was placed in solution by contact of lead-weighted silk with perspiration, saliva, urine or water. The urine and feces of four subjects wearing lead-weighted fabrics showed no excretion of lead over a period of two months. This study would seem to indicate that the wearing of lead-weighted fabrics involves practically no danger.

Other Substitutes for Tin

Basic aluminum nitrate has been suggested as a weighting agent for silk. The fabric is immersed in a fairly concentrated solution of this compound, washed, and then fixed with a solution of sodium phosphate or sodium silicate. It is claimed that an increase in weight of about 15 per cent per cycle is obtained with this procedure.

Recent studies, as yet unpublished, indicate that antimony trichloride may profitably be substituted for tin tetrachloride in the weighting of silk. It is believed that this method will make it possible to add an equal amount of weight to the silk in fewer treatments with antimony than with tin. Also the application of the antimony solution will be more in the nature of a quick padding, rather than a lengthy immersion, thus making possible a substantial reduction in the time required for weighting.

The Chemistry of Weighting Silk with Tin

The mechanism of the tin weighting process has received the attention of a number of investigators. As a result of investigations made prior to the period covered by this survey, it is assumed that silk has the property of forming an additive compound with stannic chloride. This addition compound is subsequently hydrolyzed, releasing the chlorine as free hydrochloric acid, and leaving stannic oxide ($Sn\ O_2$) combined with the silk. It has been shown that silk thus treated, gives X-ray spectrograms which are characteristic of both silk and tin oxide. If over 30% of stannic oxide is present, the silk spectrogram is masked.

In the subsequent treatments with sodium phosphate and sodium silicate the stannic acid is first changed into stannic hydroxide by the alkaline solution, and this compound enters into a reaction with the sodium phosphate and the sodium silicate. The exact composition of the resultant tin silico-phosphate has never been definitely determined. It has been shown that a secondary reaction takes place in both the phosphate and the silicate baths: namely, an interaction between the tin on the fiber and the alkali in the solution, causing a small amount of tin to go into solution as sodium stannate.

Although recent publications have not offered any radical change in the basic theories of tin weighting as stated above, several interesting contributions to this subject have been made. One paper reports the effect of weighting upon the solubility of the fibroin in concentrated salt solutions, and in the behavior of the solutions thus formed. It was found that after boiling for 20 minutes in a concentrated solution of hydrated calcium chloride ($CaCl_2.6H_2O$), unweighted silk was completely dissolved, whereas silk weighted 25% above par left an insoluble residue amounting to 47% of the original. The pure silk formed a sticky, viscous mass as it went into solution. The weighted silk left a more or less brittle insoluble portion which readily fell apart when the solution was diluted with water. A study of the absorption spectra of the fibroin solutions showed that absorption in the ultraviolet decreased more with dilution and with exposure to light in the weighted than in the unweighted silk. Other papers dealt with improvements in the weighting procedure on one hand, and in the methods of analysis for weighted silks on the other hand. For example, attention has been given to the pH values of aqueous extracts of silk weighted with tin salts. It was found that in the case of weighted silks which had become brittle, the pH values of the aqueous extracts were quite low, ranging from 2.8 to 3.9.

Again another investigator claims that the purpose of the aftertreatment with silicate is to obtain more even dyeing of the weighted silk. Greater weighting efficiency was obtained from the silicate solution at 70° C. than at either higher or lower temperatures. However, it is doubtful if the quality of the silk would be satisfactory if it was treated with silicate at temperatures much above 60° C. The addition of ammonia to the silicate bath decreases its efficiency. Wetting agents, such as sulfonated fatty alcohols, do not improve the evenness appreciably.

In connection with the analysis of weighted silks, it was found that a complete quantitative removal of the weighting could be effected by repeated extractions with hot water, a 2% solution of sodium carbonate, and a solution containing 2% of hydrochloric acid and 2% of hydrofluoric acid. Satisfactory qualitative tests have been developed for aluminum, lead, tin, zinc, phosphate and silicate.

Studies of Weighted Silks

In the previous article on silk weighting mentioned at the beginning of this chapter, it was reported that the wearing qualities of weighted silks depended to a large extent on the amount of the weighting. Lightly weighted silks have been stored for a period of three years with but very little loss in tensile strength, whereas heavily weighted silks lost over half of their tensile strength after being stored for only one year.

Recent investigations at the Ohio Agricultural Experiment Station reveal that the change in bursting and breaking strengths of weighted and unweighted silks is very similar after exposure to the Fadeometer for 6 hours. After longer exposures the unweighted silk is distinctly superior. The Fadeometer exposure causes less change in the bursting than in the breaking strengths of both types of silk. Weighted silks are stronger when wet than when dry, whereas unweighted silks are stronger dry than wet. Laundering increases the strength of weighted silks up to a certain extent.

It has been claimed that aftertreatment with thiourea increases the initial tensile strength and elasticity of weighted silk, and materially decreases the tendering which would normally take place through long periods of storage. A recent United States Patent claims that a final treatment in a basic bath, such as a solution of disodium phosphate, tends to prolong the life of weighted and dyed silk fibers.

(To be continued)

COPPER IN TEXTILE TECHNOLOGY

(Continued from page 312)

to 68 per cent nickel. Manganese iron and carbon are also present in small amounts.

The primary property of this "alloy" is its resistance to corrosive influences, and its suitability for chemical plant. Although it contains copper, the mixture does not behave like copper; for example, peroxide bleaching may be safely conducted in it. The heat conductivity of Monel is much lower than copper which is well known to be a good conductor. It is claimed that Monel, however, forms no "Air-films" between the vessel side and the liquid and hence is, in effect, a better heat conductor.

Copper has a curious property of rendering iron and steel more resistant to corrosion, the effect with 0.25 per cent addition of copper being quite marked. It also improves the resistance to acids, for example, vitriol.

A recent application of copper in the form of cuprous oxide is for rectifying alternating currents. Dry rectifiers are cleaner and much more convenient than the wet type and are much used to-day in radio receivers.

● LAUNDER-OMETER BOOKLET

The Atlas Electric Devices Company has just published a new bulletin on the Launder-Ometer, the Laboratory Washing Machine. It contains a story of the development of the machine through the cooperation with the A. A. T. C. & C. and gives methods for carrying out the various tests possible with this apparatus. The mechanical details and operation are also discussed. A list of some users of the Launder-Ometer is given. Copies of this bulletin may be obtained on request.

OPEN FORUM

Rules under which this department of the REPORTER is conducted are as follows:

1. Anyone who has a technical problem on which he would like advice may submit it to the Reporter and it will be published in the first available issue.

2. Any reader who feels that he has a solution of the problem may forward his reply to us and if we feel that the reply is suitable it will be published in a succeeding issue.

3. For each such reply published the Reporter will pay a minimum of $2.

4. In case there is more than one answer to the same question, the one covering the subject in the most complete and authentic manner will be published, or if two answers are sufficiently different both will be published. If two answers are considered equally good, the one first received will be given priority.

5. The Reporter will assume no responsibility whatsoever for the accuracy of the answers submitted—it is simply offering a vehicle for the public expression of its readers' opinions.

6. Both the questioner and answerer must send in his complete name and address. When requested we will publish only the initials or other identifying insignia.

Answers

6—I would appreciate it if you could give me any definite information or refer me to a source in regard to any present developments in the use of spun glass for decorative purposes on woolens and worsteds.—**M. M.**

Answer—I was born about 1883 and when I grew up and thought to admire spun glass decorations my mother advised me not to do so as people in her time had suffered from ornaments of fine glass. I think it was made for hat plumes and presumably resulted in some accidents from fragments in eyes, nose, etc., etc. I can't seem to work up any enthusiasm for any "present developments" for above reason—W. C. D.

8—Please give me a method for stripping of all dyes from old woolen garments, mainly sweaters.—**D. W. C.**

Answer—To strip all dyes from old woolen garments, mainly sweaters, first remove the loose color by heating to 180° F. with ammonia 28 degree using from 3% to 5% on weight of goods. Drain thoroughly. Wash with warm water until clear, repeat if necessary using 2% ammonia. In a wooden barrel mix 3% to 5% basic zinc sulfoxalate formaldehyde with an equal amount of 28% acetic acid and about 5 gals. hot water, stir and mix thoroughly; add this solution to the material to be stripped. Heat to boiling and boil 20 minutes. Add 3% more acetic acid and boil 15 minutes; drain and wash thoroughly to completely remove the stripping compound.—B. E. F.

New Questions

9—I am making tallow softeners on a laboratory scale. To what tests can I subject these tallow softeners in order that I ascertain if they will injure the cotton goods, become rancid, or decompose to form an objectionable compound? I am referring to softeners suitable for cotton piece goods only.—**J. E. G.**

10—We have a particularly difficult problem in holding our bleachery on a set shade of white, due partially to the standard getting soiled from handling as well as from yellowing with age.

We would like some information as to how other bleacheries hold their standard shade of white.—**M. P. C.**

11—In the dyeing and finishing of fabrics which have been treated with rubber latex, or in fabrics made from yarn which contain rubber filament, what precautions should be taken as to temperature in the dyebath and in drying?

Are there any chemicals ordinarily used in dyeing and finishing which should be avoided on account of their deteriorating effect upon the latex or rubber?

In what respects must such a process differ from the ordinary dyeing and finishing of similar material not containing any rubber?—**M. B. P.**

12—Please give me a method for dyeing ivory, stating any unusual precautions which it may be necessary to observe.—**B. T.**

13—What are the best books in the field for general knowledge of dyeing? I am not interested especially in specific cases but rather in developing an intelligent background for observation of the subject.—**D. D.**

14—Can you give me any information regarding what has been done in the development of ramie for use as a textile fiber? Do you think there is any market for it and for what uses is it particularly adaptable?—**R. M.**

● ARTISIL DIRECT YELLOW 2GP CONC.

This new yellow for the dyeing of acetates is unusual because it is not sensitive to photochemical reactions (a temporary change of shade caused by sun rays). Besides this feature it is said to be very fast to light in the usual meaning of the term. It is a good cold-dyeing color and, therefore, recommended by the manufacturer for jig-dyeing. Artisil Direct Yellow 2GP Conc. is also claimed to be level dyeing, fast to washing and white dischargeable. It is illustrated in the latest shade card No. 543d of the Sandoz Chemical Works.

● COLGATE PARTY

When the employes of Colgate-Palmolive-Peet Company recently held a "get-together" dance, to celebrate the arrival of the Chicago group in Jersey City, more than 1,000 persons—from executives to office boys—attended the party.

Prominent among the company personnel present were: S. Bayard Colgate, president; R. B. Colgate, vice-president; A. J. Lansing, vice-president; Ken R. Dyke, general advertising manager; W. R. Veale, manager toilet article sales, and Charles Hulsizer, Jersey plant superintendent.

The entire affair was staged by an employes' committee of sixty, representing the newcomers from Chicago and the old timers from the Jersey plant.

● COTTON WEEK

National Cotton Week was observed at the du Pont Exhibit on the Boardwalk in Atlantic City by a window display stressing the importance of du Pont dyestuffs in the development of cotton fabrics of style and quality. The setting depicted a garden scene, the back and one side enclosed with a three-foot painted hedge, wisteria, climbing roses, lilac bushes and simulated grass lending their charm.

National Cotton Week was also emphasized in the interior of the Exhibit by displays of drapery and upholstery fabrics from the Seneca Textile Corporation, dress fabrics from Charles Green Company, and another line of dress fabrics from Ameritex Sudanette, all divisions of Cohn-Hall-Marx. These were in a wide variety of bright colors in figures, stripes and plaids, and featured du Pont dyestuffs.

● OPEN OFFICES

Hercules Powder Company, Inc., has opened offices at 703 Fidelity-Philadelphia Building, Broad and Walnut Streets, Philadelphia, for the sale of Hercules Wood Rosin, Hercules Steam-distilled Wood Turpentine, and Hercules Steam-distilled Pine Oil.

C. H. Boys, formerly head of the company's Chicago naval stores territory, has been appointed manager of the Philadelphia office.

TAKE YOUR PICK!

● GREEN FOR FALL

Greens will be the fashion this Fall, according to Philip A. Vogelman, Director of the Color Fashion Bureau of the Onondaga Silk Company. Greens ranging from olive shades to bluish green will form a new note in the Fall color picture. This is forecast, according to Mr. Vogelman, by all authentic information now available and also by his analysis of coming trends.

Among the individual shades of green mentioned by this authority as important for Fall are Sycamore, a dark bottle-green; Hemlock, a rich blue-green; Balsam, with a slightly yellow cast; and Willow with still more yellow in its composition.

Rich browns, and dark berry shades, he said, would also be prominent in the color picture.

● 1934 FALL SILK COLORS

Rich mellowed tones, captioned *Faded Leaves,* supply an important high fashion motif in the collection of 1934 Fall Silk Colors just released in confidential card form by the Textile Color Card Association to its members.

These toned-down "feuilles mortes" shades, as they are called in French, will have high merchandising and fashion value in their adaptation to the new luxury fabrics which will prevail in the Fall mode, it was explained by Margaret Hayden Rorke, managing director of the color organization. This group of twelve new "leaf" tones, reflecting the rich gradations of Autumn foilage, include Treemoss, Leafgold, Leafrust, Tawny Leaf, Russet Leaf, Wineleaf, Leafbeige and Scarlet Leaf.

CLASSIFIED

The rate for "Position Wanted" advertisements in this column is 2 cents a word—with a minimum of 50 cents per insertion. For all other types of advertisements—i.e., help wanted, machinery or supplies for sale—the rate is $5.00 per column inch or less per insertion.

POSITION WANTED—Young man, three years' experience in dyehouse and bleachery. Hard worker, technical training for laboratory work wishes position. Can easily adapt himself to any sort of work. Write Box No. 813, American Dyestuff Reporter, 440 Fourth Ave., New York, N. Y.